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For: OXYNITRIDE PHOSPHOR AND PRODUCTION PROCESS
THEREOF, AND LIGHT-EMITTING DEVICE USING
OXYNITRIDE PHOSPHOR

VERIFICATION OF ENGLISH TRANSLATION

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Sir:

I, Keiichi GONJOU, declare that I am conversant in both the Japanese and English languages and that the English translation as attached hereto is an accurate translation of Japanese Patent Application No. 2002-301637 filed October 16, 2002.

Signed this 23rd day of May, 2008


Keiichi GONJOU

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Item: Drawings	1 copy
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[DOCUMENT] Specification

[TITLE OF THE INVENTION]

LIGHT-EMITTING DEVICE USING OXYNITRIDE PHOSPHOR

[CLAIMS]

[CLAIM 1]

A light-emitting device comprising:

an excitation light source and a phosphor converting the wavelength of at least the portion of light from said excitation light source,

wherein an oxynitride phosphor having the luminescence peak wavelength at a blue green to yellow region is contained in said phosphor.

[CLAIM 2]

The light-emitting device according to claim 1, wherein the oxynitride phosphor has at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf, and a rare earth element being as an activator.

[CLAIM 3]

The light-emitting device according to claims 1 or 2, wherein the oxynitride phosphor contains O and N and a weight ratio of O and N is set so that N is within a range of 0.2 to 2.1 per 1 of O.

[CLAIM 4]

The light-emitting device as in one of claims 1-3, wherein the oxynitride phosphor is represented by a general formula of $L_xM_yO_zN_{((2/3)X+(4/3)Y-(2/3)Z)}:R$ (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV-elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, and $1.5 < Z < 2.5$).

[CLAIM 5]

The light-emitting device as in one of claims 1-3, wherein the oxynitride phosphor

is represented by a general formula of $L_xM_yQ_zO_{N((2/3)X+(4/3)Y+T-(2/3)Z):R}$ (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, $0 < T < 0.5$, and $1.5 < Z < 2.5$).

[CLAIM 6]

The light-emitting device according to claims 4 or 5, wherein said X, said Y and said Z are X = 1, Y = 2, and Z = 2.

[CLAIM 7]

The light-emitting device as in one of claims 1-6, wherein 70 weight % or more of said R is Eu.

[CLAIM 8]

The light-emitting device as in one of claims 1-7, wherein 50 weight % or more of the oxynitride phosphor is crystal.

[CLAIM 9]

The light-emitting device as in one of claims 1-8, wherein the oxynitride phosphor an excitation spectrum which has a luminescence intensity excited by light of 370nm higher than luminescence intensity excited by light of 500nm.

[CLAIM 10]

The light-emitting device according to claim 1,
wherein said excitation light source has at least one or more of luminescence peak wavelengths in a range of a short wavelength side region of visible light to ultraviolet.

[CLAIM 11]

The light-emitting device according to claims 1 or 10,
wherein said excitation light source is a light-emitting element.

[CLAIM 12]

The light-emitting device according to claim 11,

wherein a light emitting layer of said light-emitting element has a nitride semiconductor containing In.

[CLAIM 13]

The light-emitting device according to claim 1,
wherein said phosphor includes a second phosphor together with said oxynitride phosphor, said second phosphor carrying out the wavelength conversion of at least a portion of light from said excitation light source and having a luminescence spectrum including one or more peak wavelengths in visible region.

[CLAIM 14]

The light-emitting device according to claim 13,
wherein said second phosphor has a luminance spectrum including at least one or more luminescence peak wavelengths from a blue region to green region, yellow region, red region.

[CLAIM 15]

The light-emitting device according to claims 13 or 14,
wherein a light mixed of at least two or more lights of a portion of a light from said excitation light source, a light from said oxynitride phosphor and a light from said second phosphor.

[CLAIM 16]

The light-emitting device as in one of claims 13 to 15,
which has a luminescence color being set at an intermediate luminescence color from the peak wavelength of said excitation light source to the peak wavelength of said oxynitride phosphor or the peak wavelength of said second phosphor.

[CLAIM 17]

The light-emitting device according to claim 16,
wherein the intermediate luminescence color is white color.

[CLAIM 18]

The light-emitting device as in one of claims 13 to 17,

wherein the luminescence spectrum has at least one or more of luminescence peak wavelengths in the ranges consisting of a range of 430 to 500nm and a range of 500 to 730nm.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[TECHNICAL FIELD TO WHICH THE INVENTION PERTAINS]

The present invention relates to a phosphor which emits a light by being excited by light, electromagnetic waves such as X-rays, electron beam, and specifically, relates to a light-emitting device for usual illuminations such as a fluorescent lamp, illuminations mounted on a car, back lights for liquid crystal, displays and the like. Specifically, the present invention relates to a white color and multi-color light-emitting device using a semiconductor light-emitting element.

[0002]

[PRIOR ART]

A light-emitting device using light-emitting elements is a small size and superior in electric power efficiency, and emits fresh color. Further, said light-emitting elements have characteristics that there is no fear of a burnt-out light bulb because of a semiconductor element and they are superior in initial drive property and resistant in vibration and the repetition of on-off lighting. Since the light-emitting elements have such superior characteristics, a light-emitting device using semiconductor light-emitting elements such as an LED and a LD has been utilized as various light sources.

[0003]

There is developed a light-emitting device which emits a luminescence color different from the light of the light-emitting elements by partially or wholly converting the wavelength of the light of the light-emitting elements and mixing said wavelength-converted light with the light of light-emitting elements not subjected to wavelength conversion to release light.

[0004]

Among these light-emitting devices, a white color light-emitting device has been required in wide fields such as usual illuminations such as a phosphorescent lamp, illuminations mounted on a car, displays and back lights for liquid crystal. Further, there is required a light-emitting device having various color tastes such as a pastel color by combining a semiconductor light-emitting element and a phosphor.

[0005]

The luminescence color of a light-emitting device using a white color semiconductor light-emitting element is obtained by the theory of color mixture. Blue light released from a light-emitting element is irradiated in a phosphor layer, then repeats absorption and scattering several times in the layer, and then, is released to outside. On the other hand, the blue light absorbed in the phosphor works as an excitation light source and emits yellow fluorescent light. The mixture of the yellow light and the blue light is visualized as white to human eyes.

[0006]

For example, a blue color light-emitting element is used as the light-emitting element, and a phosphor is thinly coated on the surface of said blue color light-emitting element. Said light-emitting element is a blue color light-emitting device using an InGaN-base material. Further, the phosphor uses a YAG-base phosphor represented by the composition formula of $(Y,Gd)_3(Al,Ga)_5O_{12}:Ce$.

[0007]

However, a white color light-emitting device equipped with the blue color light-emitting element and the YAG-base phosphor emits white color light formed by the color mixture of blue light nearby 460nm and yellow green light nearby 565nm, but luminescence intensity nearby 500nm is insufficient.

[0008]

Various phosphors are developed as the phosphor used in said light-emitting device.

[0009]

For example, an oxide-base phosphor using a rare earth metal element for a luminescence center has been widely known, and a portion of the phosphor is already practically used. However, a nitride phosphor and an oxynitride phosphor are seldom studied, and a study report is scarcely reported. For example, there is an oxynitride glass phosphor which is represented by $\text{Si}\cdot\text{O}\cdot\text{N}$, $\text{Mg}\cdot\text{Si}\cdot\text{O}\cdot\text{N}$, $\text{Ca}\cdot\text{Al}\cdot\text{Si}\cdot\text{O}\cdot\text{N}$ and the like (JP-A-2001-214162 : hereinafter, referred to as the patent literature 1). Further, there is an oxynitride glass phosphor represented by $\text{Ca}\cdot\text{Al}\cdot\text{Si}\cdot\text{O}\cdot\text{N}$ in which Eu was activated (JP-A-2002-76434 : hereinafter, referred to as the patent literature 2).

[0010]

[Patent Document 1] JP-A-2001-214162

[Patent Document 2] JP-A-2002-76434

[0011]

[PROBLEM TO BE SOLVED BY THE INVENTION]

However, conventional phosphors have low luminescence brightness and are insufficient for being used for a light-emitting device. In a light-emitting device using light-emitting elements at a near ultraviolet region as an excitation light source, there is used double step excitation that a blue light-base phosphor is excited by said light-emitting elements and the YAG-base phosphor is excited by said excited light, therefore while light having high efficiency is hardly obtained. Accordingly, there is desired a phosphor emitting green light to yellow light whose wavelength was directly converted by light of visible light at a short wavelength side region.

[0012]

Further, a white color light-emitting device combining a phosphor and a light-emitting element of visible light at a short wavelength side region is not produced yet and the light-emitting device practically used is not commercially available. Accordingly, a phosphor which efficiently emits light at a short wavelength side region of visible light is desired.

[0013]

Further, the above-mentioned oxynitride phosphors and the like described in the patent literatures 1 and 2 have low luminescence brightness and are insufficient for being used for the light-emitting device. Further, since the oxynitride glass phosphor is a glass body, it is hardly processed in general.

[0014]

Accordingly, an object of the present invention is to provide a phosphor which is excited by an excitation light source at an ultraviolet to visible light region and which has a blue green to yellow luminescence color that is wavelength converted, and to provide a light-emitting device using thereof. Further, the purpose of the present invention is to provide a light-emitting device having high luminescence efficiency and being superior in reproducibility.

[0015]

[MEANS FOR SOLVING PROBLEM]

To solve aforementioned problem, the first light-emitting device related to the present invention is a light-emitting device having an excitation light source and a phosphor converting the wavelength of at least the portion of light from said excitation light source, wherein the oxynitride phosphors having the luminescence peak wavelength at a blue green to yellow region are contained in the fore-mentioned phosphor. With this, the light-emitting device having high luminescence efficiency can be provided. Even if the YAG-base phosphor having the luminescence peak wavelength at a yellow system is emitted using the ultraviolet or near ultraviolet excitation light, it hardly emits light, but the oxynitride phosphors related to the present invention emit light by the excitation light in a range from ultraviolet to a short wavelength side region of visible light, and exhibit the high luminescence efficiency.

[0016]

Wherein the range from ultraviolet to the short wavelength side region of visible light is not specifically limited, but means a region of 240 to 500nm or less. In particular, a range of 290 to 470nm is preferable. A range of 340 to 410nm is more preferable.

[0017]

The blue green to yellow red region is represented according to JIS Z8110. Specifically, the blue green to yellow red region means a range of 485 to 610nm.

[0018]

It is preferable that the oxynitride phosphor is an oxynitride phosphor containing at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf, and a rare earth element being an activator, R. The oxynitride phosphor which contain said elements is excited by the excitation light source emitting a light in a range from near ultraviolet to a short wavelength side region of visible light and absorbs a part of the light of the excitation light source. The oxynitride phosphor converts the wavelength. The converted light has a luminescence peak wavelength at a blue green to yellow region. With this, the oxynitride phosphor can absorb a part of the light from the light emitting element and has a luminescence spectrum having a luminescence peak at a blue green to yellow region. The oxynitride phosphor has a high emission efficiency, thereby emitting a light efficiently. The light emitting device which emits a light with intermediate color in a range from a emission color of the light emitting element to a emission color of the oxynitride phosphor can be provided.

[0019]

It is preferable that the oxynitride phosphor contains O and N in the composition and the weight ratio of said O and said N so that N is within a range of 0.2 to 2.1 per 1 of O. The oxynitride phosphor can be efficiently excited by light from an excitation light source and has a luminescence color at a blue green to yellow region and high luminous efficiency.

[0020]

The oxynitride phosphor is represented by the general formula, $L_xM_yO_zN_{((2/3)x+(4/3)y-(2/3)z)}:R$ or $L_xM_yQ_zO_zN_{((2/3)x+(4/3)y+(1/3)z)}:R$ (L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge,

Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < X < 1.5$, $1.5 < Y < 2.5$, $0 < T < 0.5$, and $1.5 < Z < 2.5$. The oxynitride phosphor is excited by light in a range from near ultraviolet to a short wavelength side region of visible light and has a luminescence peak at a blue green to yellow region. The oxynitride phosphor has a stability same as or more than YAG phosphor. In addition, since the oxynitride phosphor is not glass (amorphos) but powder or particles having a crystal as a emission portion, it can be made easily. Said X, Y, T, Z set in fore-mentioned range make it possible to provide a phosphor having a high emission efficiency. That is, a crystal layer with efficient emission is formed in said range. The emission efficiency is lowered out of said range.

[0021]

The fore-mentioned X, the fore-mentioned Y and the fore-mentioned Z are preferably $X = 1$, $Y = 2$, and $Z = 2$. The more crystalline phases are formed at said composition, their crystallinity can be bettered, and the luminescence efficiency can be enhanced.

[0022]

It is preferably that Eu is 70% by weight or more among fore-mentioned R. Eu of said range makes it possible to obtain high luminescence efficiency.

[0023]

The oxynitride phosphor related to an oxynitride phosphor which has a crystal by 50% by weight or more. The crystal is preferably contained by 50% by weight or more, and more preferably by 80% by weight or more. Namely, the crystalline phases are a principal luminescent portion, and when the portion of the crystalline phases being the luminescent portion is 50% by weight or more, luminescence with good efficiency is obtained. Thus, the more the crystalline phases are, the higher the luminescence brightness can be enhanced. Further, when the portion of the crystalline phases is much, its production and processing come to be easy.

[0024]

The oxynitride phosphors preferably have the excitation spectra in which luminescence intensity by light of 370nm is higher than luminescence intensity by light of 500nm. When they are set thus, the phosphors excited by light at an ultraviolet region exhibit higher brightness than the phosphors excited by light at a blue region. The use of light-emitting elements at an ultraviolet region can constitute a light-emitting device which can exhibit higher luminescence efficiency than the use of light-emitting elements at a blue region.

[0025]

The aforementioned excitation light source has at least one or more of luminescence peak wavelengths in a range from ultraviolet to a short wavelength side region of visible light. Because the luminescence efficiency of the fore-mentioned phosphors can be enhanced by using the excitation light source having said range. In particular, the excitation light sources having the luminescence peak wavelengths at 240 to 470nm are preferably used, and among these, the excitation light sources having the luminescence peak wavelengths at 350 to 410nm are preferably used.

[0026]

The fore-mentioned excitation light source is preferably light-emitting elements. Namely, the light-emitting elements are small size, have good electric power efficiency, and emit bright color light. Further, said light-emitting elements have no fear of a burnt-out light bulb because of a semiconductor element. Further, they have characteristics that they are superior in initial drive property and resistant in vibration and the repetition of on-off lighting. Accordingly, it is preferable in the present invention to combine the light-emitting elements with the oxynitride phosphors.

[0027]

The luminescent layer of the fore-mentioned light-emitting elements has preferably a nitride semiconductor containing In. The light-emitting elements release light having the luminescence peak wavelengths at 350 to 410nm, and the fore-mentioned

oxynitride phosphors are efficiently excited by the light from said light-emitting elements to exhibit a fixed luminescence color. Since the luminescence with high intensity is obtained by being excited by light nearby 350 to 410nm, the light-emitting elements at said wavelength region are suitable. Further, since the light-emitting elements can make the width of the luminescence spectra narrow, the oxynitride phosphors can be efficiently excited, and light substantially having no color tone change can be released from the light-emitting device.

[0028]

The light-emitting devices related to a light emitting device which include the second phosphor together with the fore-mentioned oxynitride phosphors as the fore-mentioned phosphor. The second phosphor preferably carries out the wavelength conversion of at least the portion of light from the fore-mentioned excitation light sources and the fore-mentioned oxynitride phosphors. Thus, there can be provided the light-emitting device having a luminescence color at a visible light region by the color mixture of the light from the fore-mentioned excitation light sources, the fore-mentioned oxynitride phosphors and light from the second phosphor. The light-emitting device thus constituted can release a desired luminescence color so far as it is within a wavelength region from the luminescence color of the excitation light sources to the luminescence color of the oxynitride phosphors or the luminescence color of the second phosphor.

[0029]

The second phosphor may have at least one or more of the luminescence peak wavelengths from a blue region to green, yellow and red regions in order to realize a desired luminescence color (the luminescence color as the light-emitting device). In particular, various luminescence colors can be realized by combining three primary colors of the green color of the oxynitride phosphors which were excited by the excitation light sources having the luminescence peak wavelengths in a range from ultraviolet to a short wavelength side region of visible light, with the blue color and red color of the second phosphor. Further, the light-emitting device may be a light-emitting device comprising

the combination of 2 kinds of colors such as a green color with red color and a green color with yellow color.

[0030]

The fore-mentioned second phosphor is preferably at least one or more selected from an alkali earth halogen apatite phosphor, an alkali earth metal borate halogen phosphor, an alkali earth metal aluminate phosphor, an alkali earth silicate, an alkali earth sulfide, an alkali earth thiogallate, an alkali earth silicone nitride, and a germanic acid salt which are mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn; or a rare earth aluminate and a rare earth silicate which are mainly activated by the Lanthanide series element such as Ce; an organic and organic complex which are mainly activated by elements such as the Lanthanide series element such as Eu. The light-emitting device having the high luminescence brightness and high luminescence efficiency such as quantum efficiency can be provided thereby. Further, the light-emitting device having good color rendering can be provided. Provided that the second phosphor is not limited by the above descriptions, and can use phosphors which emit light having various color tastes.

[0031]

The light-emitting device releases preferably light by mixing at least 2 or more of lights among the portion of the light from the fore-mentioned excitation light source, the light from the fore-mentioned oxynitride phosphor and the light from the fore-mentioned second phosphor. The luminescence color of the light-emitting device is adjusted thereby, and a desired luminescence color can be released. In particular, when the light-emitting elements which emit light at an ultraviolet region are used, the luminescence color at the ultraviolet region can be hardly viewed by human eyes. Accordingly, the luminescence color by mixing the light from the fore-mentioned oxynitride phosphor and the light from the fore-mentioned second phosphor is exhibited. Since said luminescence color is determined only by the phosphor, the adjustment of the luminescence color is extremely carried out easily. Wherein the phosphor is represented as the second phosphor, but the

second phosphor is not limited to only one kind, and several kinds of phosphors may be contained. The finer chromaticity adjustment is possible by containing several kinds of phosphors. Further, in particular, when the light-emitting elements at a short wavelength region from ultraviolet to visible light are used, the lights from said light-emitting elements are little felt as a color taste for human eyes, therefore the deviation of chromaticity caused by production deviation can be lessened.

[0032]

The light-emitting device can have an intermediate luminescence color from the peak wavelength which the fore-mentioned excitation light source has, to the peak wavelength which the fore-mentioned oxynitride phosphors have, or the peak wavelength which the fore-mentioned second phosphor has. The excitation light source has the luminescence spectrum at a shorter wavelength side than the oxynitride phosphors or the second phosphor, and has high energy. The light-emitting device containing the fore-mentioned second phosphor can release the luminescence color from the high energy region to the low energy region of the oxynitride phosphors and the second phosphor. In particular, it exhibits the luminescence color from the luminescence peak wavelength of light-emitting elements to the first luminescence peak wavelength of the oxynitride phosphors, or the second luminescence peak wave which the second phosphor has. For example, when the luminescence peak wavelength of the light-emitting elements is situated at a blue region, the luminescence peak wavelength of the oxynitride phosphors excited is situated at a green region, and the luminescence peak wavelength of the second phosphor excited is situated at a red region, a white luminescence color can be exhibited by the color mixture of three colors. As a different example, when the luminescence peak wavelength of the light-emitting elements is situated at an ultraviolet region, the luminescence peak wavelength of the oxynitride phosphors excited is situated at a green region, and the luminescence peak wavelengths of the second phosphor excited are situated at yellow and red regions, a slightly yellowish white luminescence color and a multi-color base luminescence color can be realized. The luminescence color from a color

taste nearby the luminescence color of the oxynitride phosphors, to a color taste nearby the luminescence color of the second phosphor can be realized by changing the compounding amount of the oxynitride phosphors and the second phosphor. Further, when the second phosphor has 2 or more of the luminescence peak wavelengths, there is realized the light-emitting device exhibiting a luminescence color between the luminescence peak wavelength which the light-emitting elements have, the luminescence peak wavelength which the oxynitride phosphors have, and 2 or more of the luminescence peak wavelengths which the second phosphor has. The second phosphor is not only used alone, but also 2 or more can be used in combination. Not only a light-emitting device emitting white light but also a light-emitting device emitting light with various color tastes such as a pastel color have been recently desired. According to the light-emitting device of the present invention, there can be provided the light-emitting device having a desired color taste by variously combining the oxynitride phosphors which emit green light, the phosphor which emits red light, and the phosphor which emits blue light. In the light-emitting device related to the present invention, various color tastes can be realized not only by a process of changing the kind of phosphors, but also by a process of changing the compounding ratio of phosphors combined, a process of changing the coating process of phosphors on an excitation light source, a process of adjusting the lighting time of an excitation light source, and the like.

[0033]

It is preferable that the fore-mentioned intermediate luminescence color is a white color system. It is preferable the white color is nearby the locus of black body radiation in particular. The white color base light-emitting device can be used for various uses such as illuminations, the back light of liquid crystal and displays.

[0034]

The fore-mentioned light-emitting device has preferably the luminescence spectrum having one or more of the luminescence peak wavelengths at least at 430 to 500nm and 500 to 730nm. There can be provided the light-emitting device which emits

light having a desired color taste by combining blue light, green light and red light. Accordingly, the color rendering can be improved by combining several phosphors. In case of the same white color luminescence, there exist also a yellowish white color and a bluish white color. Accordingly, the light-emitting device has the luminescence spectrum having the luminescence peak wavelength within the above-mentioned range.

As described above, the light-emitting device related to the present invention has technical meanings that the oxynitride phosphors which are excited by the light-emitting elements at an ultraviolet to visible light region and in which the wavelength is converted are used and an excellent light-emitting device can be provided. Said oxynitride phosphors have high luminescence efficiency and are stable phosphors with high reproducibility. Further, the light-emitting device has a technical meaning that a light-emitting device having a desired luminescence color by combining the light-emitting elements, the oxynitride phosphors and the second phosphor can be provided.

[0035]

[MODE FOR CARRYING OUT THE INVENTION]

The light-emitting device related to the present invention and the oxynitride phosphor used for said light-emitting device, and the production process are illustrated below using the modes of operation and Examples. Provided that the present invention is not limited to embodiments and examples.

[0036]

The light-emitting device related to the present invention is a light-emitting device has at least a light-emitting element and the first phosphor converting the wavelength of at least the portion of light from said light-emitting element. The specific light emitting device will be described as an Example refer to Fig. 1. Fig. 1 is a section view showing the constitution of the light-emitting device related to the present invention. The relation between the name of color and the chromaticity coordinate is according to JIS Z8110.

[0037]

(Excitation light source)

An excitation light source which has at least one or more of luminescence peak wavelengths in a range of a short wavelength side region of visible light to near-ultraviolet. The excitation light source which has the luminescence peak wavelengths in said range can be used without limitation. While a lamp and a semiconductor light emitting element are given as the excitation light source, it is preferable that the semiconductor light emitting element is used.

[0038]

(Light emitting element)

The light-emitting device of Embodiment 1 is composed of a semiconductor layer 2 laminated on a sapphire substrate 1, lead frames 13 electrically connected with electro-conductive wires 14 extending from positive and negative electrodes formed on the semiconductor layer 2, a phosphor 11 and a coating member 12 formed in a cup of the lead frame 13a so as to cover outer edge of the light emitting element 10 composed of the semiconductor layer 2 and the sapphire substrate 1 and a mold member 15 covering the phosphor 11 and outer surface of the lead frame 13.

[0039]

The semiconductor layer 2 is formed on the sapphire substrate 1 and the positive and negative electrodes 3 is formed on the same plane side of the semiconductor layer 2. A luminescent layer (not illustrated) is formed in the semiconductor layer 2. The luminescent layer has a spectrum of which luminescence peak wavelength is 500nm or less at an ultraviolet to blue region.

[0040]

The light-emitting element 10 is set in a die bonder, and face-up is carried out for the lead frame 13a to be die-bonded (adhered). After the die-bonding, the lead frames 13 are transferred to a wire bonder, the negative electrode 3 of the light-emitting element is wire-bonded by a gold wire with the lead frame 13a which was provided in the cup, and the positive electrode 3 is wire-bonded with another lead frame 13b.

[0041]

Then, it is transferred to a mold equipment, and the phosphor 11 and the coating member 12 are injected in the cup of the lead frames 13 with the dispenser of the mold equipment. At this time, the phosphor 11 and the coating member 12 are preliminarily mixed at a fixed proportion homogeneously.

[0042]

After coating, the lead frames 13 are immersed in a mold frame where the mold member 15 was preliminarily injected, then the mold frame is removed and a resin is cured to prepare the cannonball type light-emitting device which is shown in Fig. 1.

[0043]

(Light emitting device)

A light emitting device of Embodiment 2 different from the light emitting device of Embodiment 1 is described in detail. The light emitting device according to the present invention is shown in Fig. 2. The light-emitting device of Embodiment 2 is a surface mounting type light-emitting device. In the light-emitting device of Embodiment 2, a nitride semiconductor light-emitting element which emits light at an ultraviolet region can be used as the light-emitting element 101, and a nitride semiconductor light-emitting element which emits light at a blue region can be also used. Hereat, the light-emitting element 101 which emits light at an ultraviolet region is illustrated as an example. In Embodiment 2, the light-emitting element 101 is a nitride semiconductor light-emitting element which has an InGaN semiconductor whose luminescence peak wavelength is about 370nm as a luminescent layer. The more specific LED element structure has a structure in which a luminescent layer having a single quantum well structure including an n-GaN layer being an undoped nitride semiconductor, a GaN layer in which an Si doped n-electrode is formed to be an n-contact layer, an n-GaN layer being an undoped nitride semiconductor, an n-AlGaN layer being a nitride semiconductor and an InGaN well layer was laminated on a sapphire substrate. An AlGaN layer as an Mg doped p-clad layer and a GaN layer being an Mg doped p-contact layer are laminated in order on the luminescent

layer. {Further, a buffer layer which was obtained by growing a GaN layer at low temperature is formed on a sapphire substrate. Further, the p-semiconductor is annealed at 400°C or more after coating.} In the above-mentioned laminated structure, the surfaces of the respective p-n-contact layers are exposed on the nitride semiconductor on the sapphire substrate by etching at the same face side. An n-electrode is formed in a belt shape on the n-contact layer exposed, and a transparent p-electrode comprising a metal thin film is formed on almost the whole surface of the residual p-contact layer. Further, a pedestal electrode is formed on the transparent p-electrode in parallel with the n-electrode using a sputtering process.

[0044]

There is used the package 105 made of kovar having a concave portion at a central part and comprising a base portion in which the lead electrode 102 made of kovar was inserted to be fixed in insulating hermetic seal at the both sides of the fore-mentioned concave portion. An Ni/Ag layer is provided on the surfaces of the fore-mentioned package 105 and the lead electrode 102. The above-mentioned light-emitting element 101 is die-bonded in the concave portion of the package 105 with an Ag-Sn alloy. All of the constitution members of the light-emitting device can be made by inorganic substances by composing thus, therefore even if the luminescence released from the light-emitting element 101 was at an ultraviolet region or a visible light short wavelength region, the light-emitting device having greatly high reliability is obtained.

[0045]

Then, the respective electrodes of the light-emitting element 101 die-bonded are electrically connected with the respective lead electrodes 102 exposed from the bottom face of the package concave portion, with the Ag wire 104 respectively. After sufficiently removing moisture in the package concave portion, it is sealed with the lid 106 made of kovar which has the glass window portion 107 at a central portion to carry out seam welding. The phosphor 108 containing $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}$, $(\text{Y}_{0.8}\text{Gd}_{0.2})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ and the like is preliminarily contained in a slurry consisting of 90% by weight of nitrocellulose and 10%

by weight of γ -alumina, the mixture is coated on the back face of the transparent window portion 107 of the lid 106, and the color conversion member is constituted by curing by heating at 220°C for 30 minutes. When light is emitted from the light-emitting device thus formed, there can be prepared a light-emitting diode which can emit white light at high brightness. There can be prepared the light-emitting device which adjusts extremely easily chromaticity and is excellent in productivity and reliability, thereby. The respective constitutions of the present invention are specifically illustrated.

[0046]

The respective constitutions of the present invention are specifically illustrated.

[0047]

{Phosphor 11, 108}

The phosphor 11, 108 includes an oxynitride phosphor. The phosphor 11, 108 which includes a second phosphor in addition to the oxynitride phosphor may be used. The oxynitride phosphor related to the present invention uses a rare earth element as an activator. The oxynitride phosphor crystal contains at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn, and at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. The combination of Group II elements and Group IV elements described in the above description is arbitrary, but the combinations below are preferably used. The oxynitride phosphor of Embodiment 1 is represented by the general formula of

$L_xM_yO_zN_{((2/3)x+(4/3)y-(2/3)z)}:R$, or $L_xM_yQ_zO_{((2/3)x+(4/3)y+(1/3)z)}:R$ {Wherein L is at least one or more of Group II elements selected from the group consisting of Be, Mg, Ca, Sr, Ba and Zn. M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. O is an oxygen element. N is a nitrogen element. R is a rare earth element. $0.5 < x < 1.5$, $1.5 < y < 2.5$, $0 < z < 0.5$, and $1.5 < z < 2.5$.} The X, Y and Z set in said range make it possible to show a high brightness. Further, in the above-mentioned general formula, X, Y and Z are preferably X = 1, Y = 2, and Z = 2 to show

high brightness. The present invention is not limited to the above-mentioned range. Specifically, the oxynitride phosphor represented by $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{ZnSi}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{CaGe}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{SrGe}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{BaGe}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{ZnGe}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.5}\text{Zn}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.5}\text{Be}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Sr}_{0.8}\text{Mg}_{0.2}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{Sr}_{0.5}\text{Mg}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$, $\text{CaSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2:\text{Eu}$, $\text{SrSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2:\text{Eu}$, $\text{BaSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2:\text{Eu}$, $\text{ZnSi}_2\text{B}_{0.1}\text{O}_2\text{N}_2:\text{Eu}$, $\text{CaGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2:\text{Eu}$, $\text{SrGe}_2\text{B}_{0.01}\text{O}_2\text{N}_2:\text{Eu}$, $\text{BaGe}_2\text{In}_{0.01}\text{O}_2\text{N}_2:\text{Eu}$, $\text{ZnGe}_2\text{Al}_{0.05}\text{O}_2\text{N}_2:\text{Eu}$, $\text{Ca}_{0.6}\text{Sr}_{0.5}\text{Si}_2\text{B}_{0.3}\text{O}_2\text{N}_2:\text{Eu}$, $\text{CaSi}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{SrSi}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{BaSi}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{0.5}\text{Ba}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}:\text{Eu}$, $\text{Sr}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}:\text{Eu}$, $\text{Ba}_{1.5}\text{Si}_{2.5}\text{O}_{2.5}\text{N}_{2.7}:\text{Eu}$, $\text{Ca}_{1.0}\text{Ba}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{1.0}\text{Sr}_{0.5}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}:\text{Eu}$, $\text{Sr}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}:\text{Eu}$, $\text{Ba}_{0.5}\text{Si}_{1.5}\text{O}_{1.5}\text{N}_{1.7}:\text{Eu}$, $\text{Ca}_{0.3}\text{Ba}_{0.2}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$, $\text{Ca}_{0.2}\text{Sr}_{0.3}\text{Si}_{2.5}\text{O}_{1.5}\text{N}_3:\text{Eu}$ and the like can be used. Further, as shown here, the oxynitride phosphor of Embodiment 1 can change a ratio of O to N, and the color tone and brightness can be adjusted by changing the ratio. Further, a molar ratio of cation to anion which is shown by $(\text{L} + \text{M})/(\text{O} + \text{N})$ can be also changed, and the luminescence spectrum and intensity can be finely adjusted thereby. This can be carried out, for example, by carrying out treatment such as vacuum and removing N and O, but the present invention is not limited to this process. In the composition of the oxynitride phosphor, there may be contained at least one or more of Li, Na, K, Rb, Cs, Mn, Re, Cu, Ag and Au, and the brightness and luminescence efficiency such as quantum efficiency can be adjusted by adding these. Further, other elements may be contained so far as the properties are not damaged.

[0048]

Further, L is at least one or more of Group II elements selected from the group consisting of Mg, Ca, Sr, Ba and Zn. That is, L may be single bodies such as Ca and Sr, and may comprise the combination of a plural number of elements such as Ca and Sr, Ca and Ba, Sr and Ba, and Ca and Mg. Further, when L is the combination of plural number of elements, the composition ratio can be varied. For example, the compounding ratio can be

varied for the mixture of Sr and Ca, if necessary.

[0049]

M is at least one or more of Group IV elements selected from the group consisting of C, Si, Ge, Sn, Ti, Zr and Hf. M may be also single bodies such as Si and Ge, and may comprise the combination of a plural number of elements such as Si and Ge, and Si and C. In the present invention, the above-mentioned Group IV elements can be used but Si and Ge are preferably used. The phosphor having good crystallinity and low cost can be provided using Si and Ge.

[0050]

R is rare earth elements. Specifically, R is one or 2 or more elements selected from La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. In the present invention, Eu is preferably used among these rare earth elements. Further, Eu and at least one or more elements selected from rare earth elements may be contained. Eu is preferably contained by 70% by weight or more as R.

[0051]

Europium Eu being the rare earth elements is used as a luminescence center. The present specification, the phosphor using Eu being a typical example as the luminescence center is occasionally illustrated, but the present invention is not limited to this. Europium has mainly a divalent and trivalent energy levels. The phosphor of Embodiment 1 uses Eu²⁺ as the activator for an alkali earth metal silicone nitride being the mother body. Eu²⁺ is easily oxidized and commercially available as the composition of Eu₂O₃ in general.

[0052]

L and M of the main components can be also used as compounds thereof as the mother material. These L and M of the main components can be used as metals, oxides, imides, amides, nitrides, and various salts. Further, the elements of L and M of the main components may be preliminarily mixed to be used.

[0053]

Q is at least one or more of Group III elements selected from the group consisting of B, Al, Ga and In. Q is also used as metals, oxides, imides, amides, nitrides, and various salts. For example, they are B_2O_6 , H_3BO_3 , Al_2O_3 , $Al(NO_3)_3 \cdot 9H_2O$, AlN , $GaCl_3$, $InCl_3$ and the like.

[0054]

The nitride of L, the nitride of M and the oxide of M are mixed as the mother body materials. The oxide of Eu is mixed with said mother body materials as the activator. These are weighed so as to be the desired phosphor composition, and mixed until being homogeneous. In particular, the nitride of L, the nitride of M and the oxide of M in the mother body materials are preferably mixed at molar ratios of $0.5 < \text{the nitride of L} < 1.5$, $0.25 < \text{the nitride of M} < 1.75$, and $2.25 < \text{the oxide of M} < 3.75$. Namely, the fixed amounts of these mother body materials are weighed and mixed so as to be the composition ratio of $L_xM_yO_zN_{((2/3)X+Y-(2/3)Z-\alpha)}:R$ or $L_xM_yQ_zO_{((2/3)X+Y+T-(2/3)Z-\alpha)}:R$.

[0055]

(Production process of oxynitride phosphor)

Then, the production process of the oxynitride phosphor related to the present invention, $CaSi_2O_2N_2:Eu$ is illustrated. The present invention is not limited to the production processes below.

[0056]

The nitride of Ca, the nitride of Si, the oxide of Si and the oxide of Eu are mixed.

[0057]

Firstly, the nitride of Ca, the nitride of Si, the oxide of Si and the oxide of Eu are prepared. As these raw materials, those purified are preferably used, but those commercially available may be used. Firstly, Ca of a raw material is crushed. The Ca of a raw material is preferably used as a single body, but compounds such as an imide compound, an amide compound and CaO can be also used. Further, the Ca of a raw material may be those containing B, Ga and the like. The crushing of the Ca of a raw material is carried out in a globe box in argon atmosphere. It is preferable that the mean

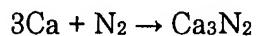
particle diameter of Ca obtained by the crushing is about $0.1\mu\text{m}$ to $15\mu\text{m}$, but is not limited to this range. The purity of Ca is preferably 2N or more, but is not limited to this range.

[0058]

Ca of a raw material is nitrided in nitrogen atmosphere. The reaction is shown in Formula 1.

[0059]

[Formula 1]



The nitride of Ca can be obtained by nitriding the Ca crushed at a temperature of 600 to 900°C for about 5 hours in nitrogen atmosphere. As the nitride of Ca, it is needless to say that those with high purity are preferable. As the nitride of Ca, those commercially available can be also used.

[0060]

Then the nitride of Ca is crushed. The crushing of the nitride of Ca is carried out in a globe box in argon atmosphere or in nitrogen atmosphere.

[0061]

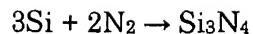
Si of a raw material is crushed. The Si of a raw material is preferably used as a single body, but a nitride compound, an imide compound, an amide compound and the like can be also used. For example, they are Si_3N_4 , $\text{Si}(\text{NH}_2)_2$, Mg_2Si , Ca_2Si , SiC and the like. The purity of the Si of a raw material is preferably 3N or more, but B, Ga and the like may be contained. The crushing of Si of a raw material is carried out in a globe box in argon atmosphere or in nitrogen atmosphere, in like manner as the Ca of a raw material. It is preferable that the mean particle diameter of the Si compound is about $0.1\mu\text{m}$ to $15\mu\text{m}$.

[0062]

The Si of a raw material is nitrided in nitrogen atmosphere. The reaction formula is shown in Formula 2.

[0063]

[Formula 2]



Silicon, Si is also nitrided at a temperature of 800 to 1200°C for about 5 hours in nitrogen atmosphere to obtain silicon nitride. It is needless to say that the silicon nitride used in the present invention is preferably those having high purity. Further, those which are commercially available can be also used.

[0064]

Then, the nitride of Si is crushed.

[0065]

As SiO_2 being the oxide of Si, those which are commercially available are used (Silicon Dioxide 99.9%, 190-09072, manufactured by Wako Pure Chemicals Industries, Ltd.).

[0066]

Raw materials which were purified or produced as above are weighed so as to be a fixed molar amount. The weighted raw materials are mixed.

[0067]

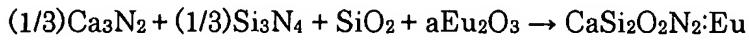
Then, the mixture of the nitride of Ca, the nitride of Si, the oxide of Si, and the oxide of Eu is calcined at about 1500°C in ammonia atmosphere. The calcined mixture is charged in a crucible to be calcined.

[0068]

The oxynitride phosphor represented by $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}$ can be obtained by mixing and calcination. The reaction formula of the basic constituting elements by the calcination is shown in Formula 3.

[0069]

[Formula 3]



[0070]

However, the composition is a typical composition deduced from the compounding ratio, and has adequate properties which are worthwhile for practical use, around the ratio.

Further, the composition of the objective phosphors can be changed by changing the compounding ratio of the respective raw materials.

[0071]

The calcination can use a tube furnace, a small size furnace, a high frequency furnace and a metal furnace and the like. The calcination temperature is not specifically limited. The calcination is preferably carried out at a temperature of 1200 to 1700°C, and a calcination temperature of 1400 to 1700°C is more preferable. It is preferable to carry out the calcination of the raw materials of the phosphor using a crucible made of boron nitride (BN) material and a boat. A crucible made of alumina (Al_2O_3) material can be also used in addition to the crucible made of boron nitride material.

[0072]

Further, reductive atmosphere is inactive gas atmospheres such as nitrogen atmosphere, nitrogen-hydrogen atmosphere, ammonia atmosphere and argon atmosphere, etc.

[0073]

The objective oxynitride phosphor can be obtained by using the above production process.

[0074]

Further, the oxynitride phosphor represented by $\text{Ca}_x\text{Si}_y\text{B}_z\text{O}_{z'}\text{N}_{((2/3)x+y+(2/3)z-z')}\text{:Eu}$ which contains B can be produced as below.

[0075]

A B compound, H_3BO_3 is preliminarily mixed with the oxide of Eu in dry condition. Europium oxide is used as the Eu compound, but metal europium, europium nitride and the like can be also used in like manner as the fore-mentioned other constitution elements. Additionally, an imide compound, a amide compound and the like can be used as the Eu compound. Europium oxide is preferably those having high purity, but those commercially available can be also used. A B compound is mixed in a dry process but a wet mixing can be also carried out.

[0076]

The production process of the oxynitride phosphor is illustrated exemplifying the B compound H_3BO_3 . However, there are Li, K, Na and the like as the component constituting elements other than B, and as these compounds, for example, there can be used $LiOH \cdot H_2O$, Na_2CO_3 , K_2CO_3 , $RbCl$, $CsCl$, $Mg(NO_3)_2$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$, $BaCl_2 \cdot 2H_2O$, $TiOSO_4 \cdot H_2O$, $ZrO(NO_3)_2$, $HfCl_4$, MnO_2 , $ReCl_5$, $Cu(CH_3COO)_2 \cdot H_2O$, $AgNO_3$, $HAuCl_4 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, GeO_2 , $Sn(CH_3COO)_2$ and the like.

[0077]

A mixture of Eu and B is crushed. The mean particle diameter of the mixture of Eu and B after the crushing is preferably about $0.1\mu m$ to $15\mu m$.

[0078]

After the above-mentioned crushing, the nitride of Ca, the nitride of Si, the oxide of Si, and the oxide of Eu containing B are mixed in like manner as the fore-mentioned production steps of $CaSi_2O_2N_2 \cdot Eu$. After said mixing, calcination is carried out and the objective oxynitride phosphor can be obtained.

[0079]

{Second phosphor 11, 108}

The second phosphor is contained together with the oxynitride phosphor as the phosphors 11 and 108. The second phosphor is preferably at least one or more selected from an alkali earth halogen apatite phosphor, an alkali earth metal borate halogen phosphor, an alkali earth metal aluminate phosphor, an alkali earth silicate, an alkali earth sulfide, an alkali earth thiogallate, an alkali earth silicone nitride, and a germanic acid salt which are mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn; or a rare earth aluminate and a rare earth silicate which are mainly activated by the Lanthanide series element such as Ce; an organic and organic complex which are mainly activated by elements such as the Lanthanide series element such as Eu. As the specific example, phosphors below can be mentioned, but the present invention is not limited to these.

[0080]

As the alkali earth halogen apatite phosphor which is mainly activated by elements such as the Lanthanide series element such as Eu and a transition metal-base element such as Mn, there are $M_5(PO_4)_3X:R$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I. R is at least one or more of Eu, Mn, and Eu and Mn.) and the like.

[0081]

As the alkali earth metal borate halogen phosphor, there are $M_2B_5O_9X:R$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I. R is at least one or more of Eu, Mn, and Eu and Mn.) and the like.

[0082]

As the alkali earth metal aluminate phosphor, there are $SrAl_2O_4:R$, $Sr_4Al_{14}O_{25}:R$, $CaAl_2O_4:R$, $BaMg_2Al_{16}O_{27}:R$, $BaMg_2Al_{16}O_{12}:R$, $BaMgAl_{10}O_{17}:R$ (R is at least one or more of Eu, Mn, and Eu and Mn.) and the like.

[0083]

As the alkali earth sulfide phosphor, there are $La_2O_2S:Eu$, $Y_2O_2S:Eu$, $Gd_2O_2S:Eu$ and the like.

[0084]

As the rare earth aluminate phosphor which is mainly activated by the Lanthanide series element such as Ce, there are YAG-base phosphors represented by the composition formulae of $Y_3Al_5O_{12}:Ce$, $(Y_{0.8}Gd_{0.2})_3Al_5O_{12}:Ce$, $Y_3(Al_{0.8}Ga_{0.2})_5O_{12}:Ce$ and $(Y, Gd)_3(Al, Ga)_5O_{12}:Ce$; and the like.

[0085]

As other phosphors, there are $ZnS:Eu$, $Zn_2GeO_4:Mn$, $MGa_2S_4:Eu$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn. X is at least one or more selected from F, Cl, Br and I.) and the like. Further, there are also $M_2Si_5N_8:Eu$, $MSi_7N_{10}:Eu$, $M_{1.8}Si_5O_{0.2}N_8:Eu$, $M_{0.9}Si_7O_{0.1}N_{10}:Eu$ (M is at least one or more selected from Sr, Ca, Ba, Mg and Zn.) and the like.

[0086]

The above-mentioned second phosphor can contain one or more selected from Tb, Cu, Ag, Au, Cr, Nd, Dy, Co, Ni and Ti, in place of Eu, or in addition to Eu if necessary.

[0087]

Further, phosphors other than the above-mentioned phosphors which have the similar performances and effects can be also used.

[0088]

As these second phosphors, there can be used phosphors which have luminescence spectra at a red color, a green color and a blue color by the excitation light of the light-emitting elements 10 and 101, and additionally, there can be also used phosphors which have luminescence spectra at a yellow color, a blue green color and an orange color which are intermediate colors. There can be produced the light-emitting device having various luminescence colors by using these second phosphors in combination with the first phosphor.

[0089]

For example, there can be provided the light-emitting device with good color rendering which emits white light by using the phosphors 11 and 108 comprising $\text{CaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ or $\text{SrSi}_2\text{O}_2\text{N}_2\text{:Eu}$ being the first phosphor which emits green to yellow light, $(\text{Sr, Ca})_5(\text{PO}_4)_3\text{Cl:Eu}$ being the second phosphor which emits blue light, and $(\text{Ca, Sr})_2\text{Si}_5\text{N}_8\text{:Eu}$. Because red, blue and green which are three primary colors of color are used, therefore a desired white light can be realized only by changing the compounding ratio of the first phosphor and the second phosphor.

[0090]

The particle diameter of the above-mentioned phosphors 11 and 108 is preferably 1 μm to 20 μm , more preferably 2 μm to 8 μm , and preferably 5 μm to 8 μm in particular. A phosphor having a particle diameter of 2 μm or less is apt to form aggregates. On the other hand, a phosphor having a particle diameter of 5 μm to 8 μm has the high absorption rate and conversion efficiency of light. Thus, the mass productivity of the light-emitting

device is improved by containing the phosphors having a large particle diameter which have optically superior properties.

[0091]

Wherein the particle diameter means the mean particle diameter obtained by an air transmission process. Specifically, a sample by 1cm³ is weighed under environments of a temperature of 25°C and a humidity of 70% and packed in an exclusive use tubular container, then dry air at fixed pressure is flown, and a specific surface area is read from differential pressure to obtain a value converted to the mean particle diameter. The mean particle diameter of the phosphors used in the present invention is preferably 2μm to 8μm. Further, the phosphor having the value of the mean particle diameter is preferably contained in high frequency. Further, those whose particle size distribution is narrow are preferable, and those having fine particles with 2μm or less are preferable in particular. Thus, the light-emitting device suppressing color unevenness and having good color tone is obtained by using phosphors having the little unevenness of the particle diameter and particle size distribution.

[0092]

The position of arranging the phosphor 108 in the light-emitting device 2 can be arranged at various positions in the positional relation with the light-emitting element 101. For example, the phosphor 108 can be contained in a mold material coating the light-emitting element 101. Further, the light-emitting element 101 and the phosphor 108 may be arranged at an interval, and the phosphor 108 may be directly mounted on the upper part of the light-emitting element 101.

[0093]

(Coating member 12, 109)

The phosphor 11,108 can be adhered using various coating members (binder) such as the resins of organic materials and glass of inorganic materials. The coating member 12 has occasionally a role as a binder for fixing the phosphor 11 on the light-emitting element 10, the window portion 107 and the like. When an organic substance is used as

the coating member (binder), as the specific material, there are preferably used transparent resins excellent in weather resistance such as an epoxy resin, an acryl resin and a silicone resin. When a silicone is used, it is preferable because it is superior in reliability and the dispersibility of the phosphor 11 can be improved.

[0094]

Further, when an inorganic substance having the similar thermal expansion coefficient as the window portion 107 is used as the coating member 12, 109 (binder), it is preferable because the phosphor 108 can be adhered on the fore-mentioned window portion 107. As the specific processes, there can be used a sedimentation process, a sol-gel process, a spray process and the like. For example, silanol ($\text{Si(OEt)}_3\text{OH}$) and ethanol are mixed with the phosphors 11 and 108 to form a slurry, the slurry is vomited from a nozzle, then the mixture is heated at 300°C for 3 hours to convert silanol into SiO_2 , and the phosphor can be fixed on a desired position.

[0095]

Further, the binding agent being an inorganic substance can be also used as the coating members (binder) 12 and 109. The binding agent is a so-called low melting point glass and fine particles, and preferably absorbs little radiation at an ultraviolet to visible region and is extremely stable in the coating members (binders) 12 and 109.

[0096]

When the phosphor having large particle diameters is adhered with the coating members (binders) 12 and 109, there are preferably used binding agents in which particles are ultra fine powder even if its melting point is high, such as for example, silica sol, alumina, or alkali earth metal pyrophosphate and phosphate having a fine particle size which is obtained by a sedimentation process. These binding agents can be used alone or they are mutually mixed to be used.

[0097]

Hereat, the coating process of the above-mentioned binding agent is described. In order to sufficiently enhance binding effect, the binding agent is preferably crushing in a

vehicle in wet condition to prepare a slurry, and used as a binding agent slurry. The fore-mentioned vehicle is a highly viscous solution which is obtained by dissolving a small amount of an adhesive binding agent in an organic solvent or deionized water. For example, an organic-base vehicle is obtained by containing 1% by weight of nitrocellulose being the adhesive binding agent based on butyl acetate being an organic solvent.

[0098]

The phosphors 11 and 108 are contained in the binding agent slurry thus obtained to prepare a coating solution. As the addition amount of the slurry in the coating solution, the total amount of the binding agent in the slurry can be 1 to 3% by weight based on the phosphor amount in the coating solution. It is preferable that the addition amount of the binding agent is little in order to suppress the lowering of a beam retention rate.

[0099]

The fore-mentioned coating solution is coated on the back face of the fore-mentioned window portion 107. Then, warm wind or hot wind is blown to dry it. Finally, baking is carried out at a temperature of 400°C to 700°C to disperse the fore-mentioned vehicle. Thus, the phosphor layer is adhered on a desired position with the binding agent.

[0100]

(Light-emitting element 10, 101)

In the present invention, the light-emitting element 10, 101 is preferably a semiconductor light-emitting element having a luminescent layer which emits light with a wavelength which can excite the oxynitride phosphor efficiently. As the material of the semiconductor light-emitting element, there can be mentioned various semiconductors such as BN, SiC, ZnSe, GaN, InGaN, InAlGaN, AlGaN, BaGaN and BInAlGaN. Further, a luminescence center can be also made by containing Si, Zn and the like in these elements as impurity elements. As the semiconductor material which can efficiently emit light at a short wavelength region among an ultraviolet region and a visible light region which can efficiently excite the phosphor 11 (oxynitride phosphor), there can be preferably mentioned

nitride semiconductors (for example, a nitride semiconductor containing Al and Ga, $In_xAl_yGa_{1-x-y}N$, $0 \leq X, Y, X+Y \leq 1$ as a nitride semiconductor containing In and Ga).

[0101]

Further, as the structure of the semiconductor light-emitting element, there are preferably mentioned semiconductors having a homo structure, a hetero structure or a double hetero structure having an MIS junction, a PIN junction, a p·n junction and the like. A luminescence wavelength can be variously selected by the material of semiconductor layers and mix crystal ratio. Further, output power can be also further improved by making a single quantum well structure and a multi quantum well structure in which a semiconductor activating layer was formed to be a thin film which generates quantum effect.

[0102]

When the light-emitting element 10,101 is composed of the nitride semiconductor, there are preferably used a substrate comprising materials such as sapphire, spinel, SiC, Si, ZnO, GaAs and GaN. The sapphire substrate is preferably used for forming the nitride semiconductor having good crystallinity by mass production. The nitride semiconductor can be formed on the sapphire substrate using a HVPE process, a MOCVD process and the like. Specifically, an amorphous buffer layer in which GaN, AlN, GaAlN and the like were grown at a low temperature is formed on the sapphire substrate, and the nitride semiconductor having a p·n junction is formed thereon.

[0103]

The preparation example of the light-emitting element capable of efficiently emitting light at an ultraviolet region which has a p·n junction using the nitride semiconductor is as below. Firstly, SiO_2 is formed in a stripe form about perpendicular to an orientation flat face of a sapphire substrate on the buffer layer. Then, ELOG (Epitaxial Lateral Over Grows GaN) growth of GaN is carried out on it using an HVPE process. Successively, the first contact layer formed with n-type GaN, the first clad layer

formed with n-AlGaN, active layers having a multi quantum well structure which laminated a plural number of layers of the well layers of InAlGaN and the barrier layers of AlGaN, the second clad layer formed with p-AlGaN, and the second contact layer formed with formed with p-GaN are laminated in order by the MOCVD process. Thus, the nitride semiconductor light-emitting element having a double hetero structure is prepared. Further, the semiconductor laser element which can be utilized for the present invention can be prepared by making the active layer be ridge stripe form, sandwiching it with guide layers, and providing the edge face of a resonator.

[0104]

Further, the nitride semiconductor exhibits an n-type conductivity in a condition in which impurities are not doped, but Si, Ge, Se, Te, C and the like are appropriately introduced as an n-type dopants in order to form an n-type nitride semiconductor having a desired carrier levels for purposes of improving the luminescence efficiency and the like. On the other hand, when a p-type nitride semiconductor is formed, Zn, Mg, Be, Ca, Sr, Ba and the like which are p-type dopants are preferably doped. Further, since the nitride semiconductor is hardly converted to p-type only by doping the p-type dopants, it is preferable to lower the resistance by heating with a furnace, plasma irradiation and the like after introducing the p-type dopants. When the sapphire substrate is not removed, the portion of the first contact layer is exposed by etching from a p-type side to the surface of the first contact layer, and electrodes are respectively formed on the respective contact layers. Then, the light-emitting elements comprising the nitride semiconductor (for example, the nitride semiconductor light-emitting element having a structure shown in Fig. 1) are prepared by cutting in a chip shape from the semiconductor wafer.

[0105]

When the phosphor 11, 108 is fixed around the surface of the light-emitting element 10 in the light-emitting device of Embodiment 2, a resin (a transparent resin) is preferably utilized for forming in good mass productivity. In this case, when both of the relation with the luminescence wavelength of the phosphor 11 and the deterioration

protection of the transparent resin are considered, the light-emitting element 10 having a luminescence spectrum at an ultraviolet region, whose luminescence peak wavelength is 360nm or more and 420nm or less, or 450nm or more and 470nm or less, is preferably used.

[0106]

Hereat, the semiconductor light-emitting element 10,101 used in the present invention is preferably adjusted so that the sheet resistance R_n of an n-type contact layer in which impurity levels are 10^{17} to $10^{20}/\text{cm}^3$ and the sheet resistance R_p of a transparent p-type electrode become the relation of the sheet resistance of $R_p \geq R_n$. The n-type contact layer is preferably formed at a film thickness of 3 to 10 μm and more preferably 4 to 6 μm , and the sheet resistance R_n is estimated to be 10 to 15 Ω/\square . Accordingly, it is preferable to set the thickness so that the sheet resistance R_p of the transparent p-type electrode is 10 to 15 Ω/\square . Specifically, the transparent p-type electrode may be formed at a thin film thickness of 150 μm or less.

[0107]

Further, when the transparent p-electrode is formed by one kind selected from a group of gold and platinum and a multilayered film or alloy comprising at least one kind of other elements, stability and reproducibility are improved by adjusting the sheet resistance of the transparent p-electrode by the content of gold or platinum element contained. Since gold or a metal element has a high absorption coefficient at the wavelength of the semiconductor light-emitting element used for the present invention, the lesser the amount of gold or platinum element contained in the transparent p-electrode is, the better the transparency is. A conventional semiconductor light-emitting element had the relation of the sheet resistance of $R_p \leq R_n$, but since it is $R_p \geq R_n$ in Embodiment 2, the transparent p-electrode is formed in a thinner film in comparison with a conventional one. The thin film forming can be easily attained by reducing the amount of gold or platinum element.

[0108]

As described above, the semiconductor light-emitting element used for the present

invention has preferably the relation of $R_p \geq R_n$ for the sheet resistance $R_n \Omega/\square$ of n-contact layer and the sheet resistance $R_p \Omega/\square$ of the transparent p-electrode. However, since it is difficult to measure R_n after preparing the semiconductor light-emitting element 10, it is substantially impossible to know the relation of R_p and R_n , but it is possible to know what relation exists between R_p and R_n from the condition of light intensity distribution at light emission.

[0109]

When the transparent p-electrode and n-contact layer have the relation of $R_p \geq R_n$, it is preferable to provide a p-side pedestal electrode having an extended conduction portion in contact with the fore-mentioned transparent p-electrode, therefore the external quantum efficiency can be further improved. The shape and direction of the extended conduction portion is not limited, and when the extended conduction portion is a linear shape, an area obstructing light is preferably reduced, but the shape may be a mesh shape. The shape may be a curve, a lattice, a branch and a hook other than the linear shape. Hereat, since the shading effect is increased in proportion to the total area of the p-side pedestal electrode, it is preferable to design the line width and length of the extended conduction portion so that the shading effect does not exceeds the luminescence increasing effect.

[0110]

{Light emitting element 10, 101}

Not only a light-emitting element emitting ultraviolet light, but also a light-emitting element emitting blue light can be also used as the light-emitting element 10, 101. The light-emitting element 10, 101 emitting blue light is also preferably Group III nitride compound light-emitting element. For example, such light-emitting element 10 has a laminated structure in which an Si undoped n-GaN layer, an n-contact layer comprising Si-doped n-GaN, an undoped n-GaN layer, a luminescent layer having a multi quantum well structure (the multi quantum well structure of GaN barrier layer/InGaN well layer), a p-clad layer comprising Mg-doped p-GaN, and a p-contact layer comprising

Mg-doped p-GaN are laminated in order on a sapphire substrate through GaN buffer layer. Further, electrodes are formed as below. Provided that the light-emitting elements different from the constitution can be also used.

[0111]

A p-Ohmic electrode is formed almost all over the surface on the p-contact layer, and a p-pad electrode is formed on the portion of the p-ohmic electrode.

[0112]

Further, the undoped GaN layer is removed from the p-contact layer by etching, the portion of the n-contact layer is exposed, and the n-electrode is formed on the exposed portion.

[0113]

Further, the luminescent layer having a multi quantum well structure was used in Embodiment, but the present invention is not limited to this. For example, it may be a single quantum well structure utilizing InGaN, and GaN to which Si, Zn and the like were doped may be utilized.

[0114]

Further, in the luminescent layer of the light-emitting element 10, the main luminescence peak wavelength can be varied within a range of 420nm to 490nm by changing the content of In. Further, the luminescence peak wavelength is not limited to the above-mentioned range, and those having the luminescence peak wavelength the luminescence peak wavelength at 360 to 550nm can be also used.

[0115]

(Coating member 12, 109)

The coating member 12 (transparent material) is provided in the cup of the lead frames 13, and used by being mixed with the phosphor 11. As the specific material of the coating member 12, there are used transparent resins excellent in temperature property and weather resistance such as an epoxy resin, a urea resin and a silicone resin; silica sol, glass, an inorganic binder and the like. Further, a dispersant, barium titanate, titanium

oxide, aluminum oxide and the like may be contained together with the phosphor.

Further, a light stabilizer and a coloring agent may be contained.

[0116]

(Lead frame 13)

The lead frame 13 is constituted by the mount lead 13a and the inner lead 13b.

[0117]

The mount lead 13a arranges the light-emitting element 10. The upper part of the mount lead 13a is a cup shape, and the light-emitting element 10 is die-bonded in the cup. The light-emitting element 10 is covered in the cup with the fore-mentioned phosphor 11 and the fore-mentioned coating member 12. Further, a plural number of the light-emitting elements 10 are arranged in the cup, and the mount lead 13a can be utilized as a common electrode of the plural number of the light-emitting elements 10. In this case, an adequate electroconductivity and the connecting property of the electroconductive wire 14 are required. The die bonding (adhesion) of the light-emitting element 10 with the cup of the mount lead 13a can be carried out by a thermosetting resin and the like. As the thermosetting resin, an epoxy resin, an acryl resin, an imide resin and the like are mentioned. Further, it is die-bonded with the mount lead 13a by the face down light-emitting element 10 and the like, and an Ag paste, a carbon paste, a metal bump and the like can be used for carrying out electric connection. Further, an inorganic binder can be also used.

[0118]

The inner lead 13b is electrically connected with the electroconductive wire 14 which is extended from the electrode 3 of the light-emitting elements 10 which were arranged on the mount lead 13a. The inner lead 13b is preferably arranged at a position which is separated from the mount lead 13a for preventing a short circuit with the mount lead 13a. When a plural number of the light-emitting elements 10 are arranged on the mount lead 13a, a constitution in which the respective wires are not mutually connected is required. The inner lead 13b uses preferably the similar material as that of the mount

lead 13a, and iron, copper, copper with iron, gold, platinum, silver and the like can be used.

[0119]

(Electroconductive wire)

The electroconductive wire 14 connects electrically the electrode 3 of the light-emitting elements 10 with the lead frame 13. The electroconductive wire 14 is preferably those having good ohmic property, mechanical connecting property and heat conductivity with the electrode 3. The specific material of the electroconductive wire 14 is preferably metals such as gold, copper, platinum, aluminum and the like, and alloys thereof, etc.

[0120]

(Mold member)

The mold member 15 is provided for protecting the light-emitting elements 10, the phosphor 11, the coating member 12, the lead frame 13, the electroconductive wire 14 and the like from the external. The mold member 15 has purposes of expanding the angle of visibility, reducing the directionality from the light-emitting elements 10, and focusing and scattering luminescence in addition to the purpose of protection from the external. In order to attain the purposes, the mold member can be formed in a desired shape. Further, the mold member 15 may be a convex lens shape, a concave lens shape, additionally, a structure in which a plural number of layers were laminated. As the specific material of the mold member 15, there can be used materials excellent in transmission property, weather resistance and temperature property such as an epoxy resin, a urea resin, a silicone resin, a silica sol, a glass, and the like. A dispersant, a coloring agent, an ultraviolet absorbent and a phosphor be contained in the mold member 15. As the dispersant, barium titanate, titanium oxide, aluminum oxide and the like are preferable. The same material is preferably used for reducing the repulsion of the coating member 12 with the material and for considering a refractive index.

[0121]

The phosphors and the light-emitting device related to the present invention are

illustrated below according to examples, but not limited to these examples.

[0122]

Further, temperature properties are shown by a relative brightness in which the luminescence brightness at 25°C is 100%. Further, the particle diameter shows the fore-mentioned particle diameter, and is a value obtained by an air transmission process called as F.S.S.S.No. (Fisher Sub Sieve Sizer's No.).

[0123]

[EXAMPLE]

The examples related to the present invention are illustrated below.

[0124]

(Phosphor)

Table 1 shows the properties of the oxynitride phosphors of Examples 1 to 5 related to the present invention.

[0125] Further, Fig. 3 is a chart showing luminescence spectra when the nitride phosphors of Examples 1 to 5 were excited at Ex = 400nm. Fig. 4 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at Ex = 460nm. Fig. 5 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 6 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5. Fig. 7 is an SEM photo photographing the oxynitride phosphor of Example 1. Hereat, the name of a color and chromaticity are according to JIS Z8110.

[0126]

Table 1

	Ex=400nm			Particle diameter (μm)
	Color tone X	Color tone Y	Peak wavelength (nm)	
Example 1	0.434	0.543	561	3.5
Example 2	0.433	0.543	561	4.0
Example 3	0.349	0.608	539	4.0
Example 4	0.352	0.604	539	3.5
Example 5	0.182	0.55	509	3.5

	Ex=460nm		
	Color tone X	Color tone Y	Peak wavelength (nm)
Example 1	0.437	0.545	564
Example 2	0.434	0.546	564
Example 3	0.347	0.616	540
Example 4	0.351	0.614	540
Example 5	0.214	0.623	510

[0127]

Example 1 is the oxynitride phosphor represented by $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}$. Example 2 is the oxynitride phosphor represented by $\text{Ca}_{0.90}\text{Mg}_{0.10}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$. Example 3 is the oxynitride phosphor represented by $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}$. Example 4 is the oxynitride phosphor represented by $\text{Sr}_{0.90}\text{Mg}_{0.10}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}$. Example 5 is the oxynitride phosphor represented by $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}$.

[0128]

Ca_3N_2 , Si_3N_4 , SiO_2 and Eu_2O_3 were used as the raw materials. The raw materials are crushed to 0.1 to 3.0 μm . After crushing following raw materials are used in the Example 1.

Ca_3N_2 : 6.01 g

Si_3N_4 : 5.99 g

SiO_2 : 7.36 g

Eu_2O_3 : 0.66 g

After weighing the above-mentioned amounts, Ca_3N_2 , Si_3N_4 , SiO_2 and Eu_2O_3 were mixed under nitrogen atmosphere in a glove box until uniformity. The concentration of Eu is 0.43% by mol in Examples 1 to 5.

[0129]

In Example 1, the mix ratio (molar ratio) of the raw materials is $\text{Ca}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.51 : 3.02 : 0.046$. 6.01g of Ca_3N_2 (molecular weight = 148.3), 5.99g of Si_3N_4 (molecular weight = 140.3), 7.36g of SiO_2 (molecular weight = 60.09) and 0.66g of Eu_2O_3 (molecular weight = 352.0) were weighed so as to be the mixing ratio, and mixed.

[0130]

The above-mentioned compounds were mixed, the mixture was charged in a boron nitride crucible in ammonia atmosphere, and calcination was carried out at about 1500°C for about 5 hours.

[0131]

The objective oxynitride phosphor was obtained thereby. The theoretical composition of the oxynitride phosphor obtained is $\text{CaSi}_2\text{O}_2\text{N}_2:\text{Eu}$.

[0132]

When the % by weight of O and N in the oxynitride phosphor of Example 1 was measured, O and N were contained by 19.3% by weight and 14.5% by weight respectively. The weight ratio of O to N is O : N = 1 : 0.75.

[0133]

The calcination of the oxynitride phosphor related to Examples is carried out in ammonia atmosphere using a boron nitride crucible. A crucible made of a metal is not preferably used for the crucible. When the crucible made of a metal is used, it is considered that the crucible is eroded and it causes the lowering of luminescence properties. Accordingly, it is preferable to use a crucible made of ceramics such as alumina.

[0134]

Example 2 is the oxynitride phosphor in which the portion of Ca was substituted with Mg. Example 2 used magnesium nitride, Mg_3N_2 (MG102PB 98%, manufactured by High Purity Chemicals Co.) (molecular weight = 101.0), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is $\text{Ca}_3\text{N}_2 : \text{Mg}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.12 : 0.57 : 3.37 : 0.052$.

$\text{Ca}_3\text{N}_2 : 5.44 \text{ g}$

$\text{Mg}_3\text{N}_2 : 0.43 \text{ g}$

$\text{Si}_3\text{N}_4 : 6.05 \text{ g}$

$\text{SiO}_2 : 7.43 \text{ g}$

$\text{Eu}_2\text{O}_3 : 0.67 \text{ g}$

Further, said raw materials were mixed and calcination was carried out under the

same conditions as Example 1.

[0135]

Example 3 is the oxynitride phosphor in which Ca of Example 1 was substituted with Sr. Example 3 used strontium nitride, Sr_3N_4 (molecular weight = 290.9), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is $\text{Sr}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.51 : 3.02 : 0.046$.

$\text{Sr}_3\text{N}_2 : 9.14 \text{ g}$

$\text{Si}_3\text{N}_4 : 4.65 \text{ g}$

$\text{SiO}_2 : 5.71 \text{ g}$

$\text{Eu}_2\text{O}_3 : 0.51 \text{ g}$

Example 3 mixed said raw materials were mixed and carried out calcination under the same conditions as Example 1.

When the % by weight of O and N in the oxynitride phosphor of Example 3 was measured, O and N were contained by 15.3% by weight and 11.2% by weight respectively in the total amount. The weight ratio of O to N is $\text{O} : \text{N} = 1 : 0.73$.

[0136]

Example 4 is the oxynitride phosphor in which Ca of Example 2 was substituted with Sr. In Example 4, the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is $\text{Sr}_3\text{N}_2 : \text{Mg}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.12 : 0.57 : 3.37 : 0.052$.

$\text{Sr}_3\text{N}_2 : 8.46 \text{ g}$

$\text{Mg}_3\text{N}_2 : 0.34 \text{ g}$

$\text{Si}_3\text{N}_4 : 4.80 \text{ g}$

$\text{SiO}_2 : 5.89 \text{ g}$

$\text{Eu}_2\text{O}_3 : 0.53 \text{ g}$

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0137] Example 5 is the oxynitride phosphor in which Ca of Example 1 was substituted

with Ba. Example 5 used barium nitride, Ba_3N_2 (molecular weight = 316.6), and the under-mentioned amounts of crushed powders were weighed so that the mixing ratio (molar ratio) of the raw materials is $\text{Ba}_3\text{N}_2 : \text{Si}_3\text{N}_4 : \text{SiO}_2 : \text{Eu}_2\text{O}_3 = 1 : 0.76 : 0.22 : 0.033$.

$\text{Ba}_3\text{N}_2 : 11.2 \text{ g}$

$\text{Si}_3\text{N}_4 : 3.77 \text{ g}$

$\text{SiO}_2 : 4.63 \text{ g}$

$\text{Eu}_2\text{O}_3 : 0.42 \text{ g}$

Said raw materials were mixed and calcination was carried out under the same conditions as Example 1.

[0138]

Any of the calcined products of Examples 1 to 5 is crystalline powder or particles. The particle diameter was about 1 to $5\mu\text{m}$.

[0139]

The measurement of the excitation spectra of the oxynitride phosphors of Examples 1 to 5 was carried out. As a result of the measurement, they are strongly excited at a shorter wavelength side than 490nm.

[0140]

The oxynitride phosphors of Examples 1 to 5 were excited by $\text{Ex} = 460\text{nm}$. Since $\text{Ex} = 460\text{nm}$ is a wavelength often used in a blue light-emitting element, excitation was carried out at said wavelength region. As a result, the oxynitride phosphor of Example 1 has a luminescence color at a yellow region of color tone, $x = 0.437$ and color tone $y = 0.545$. The oxynitride phosphor of Example 4 has a luminescence color at a yellow region of color tone, $x = 0.351$ and color tone, $y = 0.614$. Any of the oxynitride phosphors of Examples 1 to 5 exhibited higher luminescence efficiency than a conventional phosphor.

[0141]

The oxynitride phosphors of Examples 1 to 5 were excited by $\text{Ex} = 400\text{nm}$. The oxynitride phosphor of Example 1 has a luminescence color at a yellow green region of color tone, $x = 0.434$ and color tone, $y = 0.543$. The oxynitride phosphor of Example 3 has a

luminescence color at a yellow green region of color tone, $x = 0.349$ and color tone, $y = 0.608$. Any of the oxynitride phosphors of Examples 1 to 5 exhibited higher luminescence efficiency than a conventional phosphor.

[0142]

Further, temperature properties were excellent. The temperature properties are shown by relative brightness in which luminescence brightness at 25°C is 100%. The particle diameter is a value according to an air transmission process called F.S.S.No. (Fisher Sub Sieve Sizer's No.). The temperature properties of Examples 1 to 5 are 95 to 100% at 100°C. They were 65 to 90% at 200°C.

[0143]

When the X-ray diffraction images of the above-mentioned these oxynitride phosphors were measured, any image shows a sharp diffraction peak, and it was cleared that the phosphors obtained were crystalline compounds having regularity.

[0144]

<Light-emitting device>

The light-emitting device of Example 1 was produced using the above-mentioned oxynitride phosphor. A light emitting element which has a emission spectrum of 400 nm is used as an exciting source. As the phosphor, $\text{CaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 1, $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu}$ and $(\text{Ca}_{0.93}, \text{Eu}_{0.05}, \text{Mn}_{0.02})_{10}(\text{PO}_4)_6\text{Cl}_2$ are used. The light-emitting device according to the present invention is illustrated in Fig. 1. Fig. 8 is a plane view showing the light-emitting element related to the present invention. Fig. 9 is a section view showing the A-A' of the light-emitting element related to the present invention. Fig. 10 is a chart showing the luminescence spectrum of the light-emitting device of Example 1. Fig. 11 is a chart showing the chromaticity coordinate of the light-emitting device of Example 1.

[0145]

(Light-emitting element)

The substrate 201 comprising sapphire (c plane) was set in the reaction vessel of MOVPE, and the temperature of the substrate 201 was raised until about 1050°C while

flowing hydrogen to clean the substrate 201.

[0146]

Wherein a sapphire substrate is used for the substrate 201 in the present Example, but there may be used different kind substrates different from a nitride semiconductor substrate, namely nitride semiconductor substrates such as AlN, AlGaN and GaN, as the substrate 201. As the different kind substrates, for example, there can be used insulating substrate such as sapphire in which either of a C plane, R plane and A plane is a main plane, and spinel ($MgAl_2O_4$); oxide substrates which lattice-coordinate with SiC (including 6H, 4H and 3C), ZnS, ZnO, GaAs, Si and a nitride semiconductor; substrate materials which can grow a nitride semiconductor and are different from the nitride semiconductor. As the preferable different kind substrates, sapphire and spinel are mentioned. Further, the different kind substrates may be off-angled, and in this case, when a substrate which was off-angled in a stepwise shape is used, the growth of the groundwork layer 202 comprising GaN is grown in good crystallinity, therefore it is preferable. Further, when the different kind substrate is used, a nitride semiconductor which becomes the groundwork layer 202 before formation of element structure is grown on the different kind substrate, then the different kind substrate is removed by processes such as polishing, and an element structure may be formed as the single body substrate of the nitride semiconductor. Further, there may be a process of removing the different kind substrate after forming the element structure. The substrate of the nitride semiconductor such as AlN may be used in addition to a GaN substrate.

[0147]

(Buffer layer)

Successively, the temperature of the substrate 201 is lowered to 510°C, and a buffer layer (not illustrated) comprising GaN is grown on the substrate 201 at a film thickness of about 100 angstroms using hydrogen as a carrier gas and ammonia and TMG (trimethylgallium) as the raw material gases.

[0148]

(Groundwork layer)

After forming the buffer layer, only TMG is stopped, and the temperature of the substrate 201 is raised to 1050°C. When it reached at 1050°C, an undoped GaN layer is grown at a film thickness of 2μm similarly using ammonia gas and TMG as the raw material gases.

[0149]

(n-Type layer)

Successively, an n-type layer 203 comprising GaN in which Si was doped by $4.5 \times 10^{18}/\text{cm}^3$ is grown at a thickness of 3μm at 1050°C similarly using ammonia gas and TMG as the raw material gases and silane gas as impurity gas, as a n-side contact layer which forms the n-side electrode 211a as the n type layer.

[0150]

(Active layer)

A barrier layer comprising Si-doped GaN is grown at a film thickness of 50 angstroms, and successively, a well layer comprising undoped $\text{In}_{0.1}\text{Ga}_{0.7}\text{N}$ is grown at a film thickness of 50 angstroms at 800°C using TMG, TMI and ammonia. Then, 4 layers of the barrier layer and 3 layers of well layer are alternatively laminated in order of barrier + well + barrier + well + barrier + barrier, and the active layer 204 comprising a multiple quantum well structure having a total film thickness of 350 angstroms is grown.

[0151]

(p-Side carrier confining layer)

Then, the p-side carrier confining layer 205 comprising $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ in which Mg was doped by $5 \times 10^{19}/\text{cm}^3$ is grown at a film thickness of 100 angstroms using TMG, TMA, ammonia and Cp_2Mg (cyclopentadienylmagnesium).

[0152]

(The first p-layer)

Successively, the first p-layer 206 comprising GaN in which p-type impurities were doped is grown at a film thickness of 0.1μm using TMG, ammonia and Cp_2Mg .

[0153]

(The second p-layer)

As the second p-layer, a p-side contact layer 208 on whose surface a p-side electrode 210 is formed is formed. The p-side contact layer 208 is obtained by growing a p-type GaN in which Mg was doped by $1 \times 10^{20}/\text{cm}^3$ on the current diffusion layer, at a film thickness of 150 angstroms. Since the p-side contact layer 208 is a layer on which the p-side electrode 210 is formed, it is preferably a high carrier concentration with $1 \times 10^{17}/\text{cm}^3$ or more. When it is lower than $1 \times 10^{17}/\text{cm}^3$, it is apt to be difficult to obtain a preferable contact with the electrode. Further, when the composition of the contact layer is GaN, it is easy to obtain a preferable contact with the electrode material.

[0154]

After completion of the reaction forming the above element structure, the temperature is lowered to room temperature, and annealing is carried out at 700°C charging a wafer in the reaction vessel under nitrogen atmosphere, and the resistance of the p-layer is further lowered. The wafer on which the element structure was formed is taken out from the equipment, and an electrode forming step described below is carried out.

[0155]

After the annealing, the wafer is taken out from the reaction vessel, a fixed mask is formed on the surface of the p-side contact layer 208 being the uppermost layer, etching is carried out from the p-side contact layer 208 side with an RIE (reactive ion etching) equipment to expose the surface of the n-side contact layer, and an electrode forming surface is formed.

[0156]

As a p-side electrode 210, Ni and Au are laminated in order, and the p-side contact layer comprising Ni/Au is formed. Further, the p-side electrode 210 becomes an ohmic electrode which is brought in contact with the second p-layer and the p-side contact layer 208. At this time, the electrode branch 210a formed has a width of the stripe shape

luminescent portion 209 of about 5 μ m and a width of the stripe shape electrode branch 210 of about 3 μ m, and the stripe shape luminescent portion 209 and the stripe shape electrode branch 210 are alternately formed. Only the portion of the p-side electrode 210 is formed at a region where the p-pat electrode is formed, and formed over the p-pat electrode to be electrically conducted. At this time, only the portion of the p-side electrode 210 is formed at a region where the p-pat electrode is formed, the p-pat pat electrode 210b is formed on the surface of the p-side contact layer 208, the portion is formed over the p-side electrode 210 to be electrically conducted. At this time, there is obtained a structure in which the surface of the p-side contact layer 208 where the p-side pat electrode 210b is provided is not brought in contact with the p-side electrode 210 and the p-side contact layer 208, a shot key barrier is formed between both, current does not directly run in the element from the forming portion of the p-side pat electrode 210b, and current is injected in the inside of the element through the electrode branch 210a which was electrically connected.

[0157]

Successively, an n-electrode 211a is formed on the exposed plane 203a on which the n-layer 203 was exposed. The n-electrode 211a is formed by laminating Ti and Al.

[0158]

Hereat, the n-electrode 211a is an ohmic electrode which was brought in ohmic contact with the exposed face 203a of the n-type layer 203. After forming the p-side electrode 210 and the n-side electrode 211a for ohmic, the respective electrodes are brought in ohmic contact by being annealed by heat treatment. The p-side ohmic electrode which was obtained at this time becomes an opaque film which hardly transmit the luminescence of the active layer 204.

[0159]

Successively, an insulation film comprising SiO₂ is formed on the portion or the whole surface excluding the whole of the above-mentioned p-side electrode 210 and the n-side electrode 211a, namely, the insulation film comprising SiO₂ is formed on the whole element surfaces such as the exposed face 203a of the n-type layer 203 and the side face of

said exposed face 203a. After formation of the insulation film, the pat electrodes for bonding are respectively formed on the surfaces of the p-side electrode 210 and the n-side electrode 211a which were exposed from the insulation film, and electrically conducted with the respective electrodes for ohmic. The p-side pat electrode 210b and the n-side pat electrode 211b are respectively formed by laminating Ni, Ti and Au on the respective electrodes for ohmic.

[0160]

Finally, the light-emitting elements having a length of 300μm at one side are obtained by dividing the substrate 201.

[0161]

The luminescence peak wavelength is about 400nm.

[0162]

The properties of the light-emitting device of Example 28 are shown in Table 5.

[0163]

Table 2

	Current If(mA)	Voltage Vf(V)	Radiation analysis Radiometric (mW)	Luminous intensity measurement Photometric (lm)	Peak wavelength Peak (nm)
Light emitting device	20	3.4	6.2	1.84	464

Color tone x	Color tone y	Color temperature T _{cp} (K)	Average color rendering Ra	Lamp efficiency (lm/W)
0.356	0.368	4690	82.2	27.1

[0164]

The light-emitting device of Example 1 exhibits a luminescence color at a white region. The light-emitting device of Example 1 exhibits a luminescence spectrum having the luminescence peak wavelengths at 360 to 430nm, 430 to 500nm and 500 to 730nm. More specifically, it exhibits a luminescence spectrum having the luminescence peak wavelengths at 390 to 410nm, 455 to 475nm and 550 to 600nm. The phosphors excited by

the light-emitting element at 400nm excitation have respectively the luminescence peak wavelengths at a green region in case of $\text{CaSi}_2\text{O}_2\text{N}_2\text{:Eu}$ of Example 1, at a yellow to red region in case of $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu}$, and at a blue region in case of $(\text{Ca}_{0.93}, \text{Eu}_{0.05}, \text{Mn}_{0.02})_{10}(\text{PO}_4)_6\text{Cl}_2$. It exhibits a luminescence color at a white region by the color mixture of lights from these phosphors. It emits white light with various color tastes by changing the compounding amounts of these phosphors. Accordingly, when a light-emitting device having a fixed white light using ultraviolet light as an excitation light source is produced, the luminescence color can be changed by only changing the kind of phosphors, compounding ratio and the like.

[0165]

<Light-emitting device>

The light-emitting device of Example 2 is a white light-emitting device using a light-emitting element having the luminescence peak wavelength at 460nm, as an excitation light source. The light-emitting device of the present invention has also a structure shown in Fig. 1.

[0166]

Namely, in the light-emitting device of Example 2, the semiconductor layer 2 of an n-type GaN layer and p-type GaN layer is formed on the sapphire substrate 1, the electrode 3 is provided at said n-type and p-type semiconductor layers 2, said electrode 3 is electrically connected with the lead frame 13 by the electroconductive wire 14. The upper portion of the light-emitting device 10 is covered with the phosphor 11 and the coating member 12, and the outer peripheral portions of the lead frame 13, the phosphor 11 and the coating member 12 are covered with the mold member 15. The semiconductor layer 2 is obtained by laminating n⁺GaN:Si, n-AlGaN:Si, n-GaN, GaInN QWs, p-GaN:Mg, p-AlGaN:Mg, and p-GaN:Mg in order on the sapphire substrate 1. The portion of said n⁺GaN:Si is etched and an n-type electrode is formed. A p-type electrode is formed on said p-GaN:Mg layer. Copper with Fe is used for the lead frame 13. A cup for mounting the light-emitting device 10 is provided on the upper portion of the mount lead 13a, and the

light-emitting element 10 is die-bonded at about the central part bottom of said cup. Gold is used for the electroconductive wire 14, and Ni plating is carried out on the bump 4 for electrically connecting the electrode 3 with the electroconductive wire 14. As the coating member 12, a mixture which mixed an epoxy resin and a dispersant, barium titanate, titanium oxide and the fore-mentioned phosphor 11 at a fixed proportion is used. The epoxy resin is used for the mold member 15. The cannonball type light-emitting device 1 is a column in which the mold member 15 is a radius of 2 to 4mm, height is about 7 to 10mm, and the upper part is a hemisphere.

[0167]

When current is run in the light-emitting device of Example 2, the blue light-emitting element 10 having the luminescence spectrum with a peak wave length of about 460nm emits light. The phosphor 11 which covers the semiconductor layer 2 carries out the conversion of color tone. As a result, there can be provided the light-emitting device of Example 29 which emits white light.

[0168]

The phosphor 11 of the light-emitting device of Example 2 related to the present invention uses the phosphor 11 which mixed the oxynitride phosphor of Example 1 and the nitride phosphor represented by $\text{CaSrSi}_5\text{N}_8:\text{Eu}$. Said phosphor 11 is mixed with the coating member 12.

[0169]

The portion of light from the light-emitting element 10 transmits the light-emitting device of Example 2. Further, the portion of light from the light-emitting element 10 excites the phosphor 11, the phosphor 11 carries out the wavelength conversion, and red light is emitted from the green color of the oxynitride phosphor and the yellow red color of the nitride phosphor. There can be provided the light-emitting device which emits white light, by the color mixture of blue light from these light-emitting elements 10, green light from the oxynitride phosphor, and yellow red to red light from the nitride phosphor.

[0170]

<Light-emitting device>

Fig. 12 is a chart showing the cap type light-emitting device of Example related to the present invention.

[0171]

In the light-emitting device of Example 3, the same codes are imparted for the same members as those in the light-emitting device of Example 1, and illustrations thereof are abbreviated. As the light-emitting element 10, a light-emitting element having the luminescence peak wavelength at 400nm is used.

[0172]

The light-emitting device of Example 3 is constituted by covering the cap 16 comprising a transparent resin in which phosphors (not illustrated) were dispersed on the surface of the mold member of the light-emitting device of Example 1.

[0173]

A cup for mounting the light-emitting device 10 is provided on the upper portion of the mount lead 13a, and said light-emitting element 10 is die-bonded at about the central part bottom of said cup. The phosphor 11 is provided on the upper part of said cap so as to cover the light-emitting element 10 in the light-emitting device of Example 3, but the phosphor may be contained only in the cap 16 in the light-emitting device of Example 3. When the phosphor 11 is not provided on the light-emitting element 10, the phosphor is able not to directly receive the influence of heat generated from the light-emitting element 10.

[0174]

Further, the phosphor is homogeneously dispersed in a transparent resin in case of the cap 16. The transparent resin containing the phosphor is molded in a shape which is fitted for the shape of the mold member 15. Alternatively, there is also possible a process of charging the transparent resin containing the phosphor into a fixed mold, then pushing the light-emitting device 1 into said mold and molding it. As the specific example of the transparent resin of the cap 16, there are used transparent resins excellent in

temperature properties and weather resistance such as an epoxy resin, a urea resin and a silicone resin; silica sol, glass, an inorganic binder and the like. In addition to the resins mentioned above, there can be also used thermosetting resins such as a melamine resin and a phenol resin. Further, there can be also used thermoplastic resins such as a polyethylene, a polypropylene, a poly(vinyl chloride) and a polystyrene; thermoplastic rubbers such as a styrene-butadiene block copolymer and a segmented polyurethane, etc. Further, a dispersant, barium titanate, titanium oxide, aluminum oxide and the like may be contained together with the phosphor. Further, a light stabilizer and a coloring agent may be contained. The nitride phosphor of $\text{Ca}_2\text{Si}_5\text{N}_8\text{:Eu}$ and the phosphor of $(\text{Ca}_{0.95}, \text{Eu}_{0.05})_{10}(\text{PO}_4)_6\text{Cl}_2$ are used for the phosphors contained in the cap 16. The nitride phosphor of Example 3 is used for the phosphor 11 used in the cap of the mount lead 13a. However, since the phosphors are used in the cap 16, there may be a structure in which the cap 16 contains the oxynitride phosphor and only the coating member 12 exists in the cap of the mount lead 13a.

[0175]

In the light-emitting device thus constituted, the portion of light emitted from the light-emitting element 10 excites the oxynitride phosphor of the phosphor 11 and green light is emitted from the oxynitride phosphor. Further, the portion of light emitted from the light-emitting element 10 or the portion of light emitted from the oxynitride phosphor excites the phosphor of the cap 16, and red light is emitted from blue and yellow. The green light of the oxynitride phosphor is mixed with the red light from the blue color and yellow color of the phosphor of the cap 16, and as a result, white light is released from the surface of the cap 16.

[0176]

[EFFECT OF THE INVENTION]

As described above, the present invention relates to a light emitting device including a phosphor which is efficiently excited by light in a range from near ultraviolet to a short wavelength side region of visible light from an excitation light source and has a

luminescence color at a blue green to yellow region. The light emitting device shows a Hungary color. In particular, the oxynitride phosphors excited by an utter-violet light from light emitting element show a luminescent color in a range from blue to yellow region. The light emitting device which has an excellent luminescent properties can be provided by changing a composition of the oxynitride phosphor. The light emitting device of the present invention has a high luminescent efficiency and good reproducibility. Therefore, the present invention have excellent technical meanings.

[BRIEF DESCRIPTION OF DRAWING]

Fig. 1 is a view showing the cannonball type light-emitting device 1 related to the present invention;

Fig. 2(a) is a plane view showing the surface mounting type light-emitting device related to the present invention, and Fig. 2(b) is a section view showing the surface mounting type light-emitting device related to the present invention;

Fig. 3 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $Ex = 400\text{nm}$;

Fig. 4 is a chart showing the luminescence spectra when the oxynitride phosphors of Examples 1 to 5 were excited at $Ex = 460\text{nm}$;

Fig. 5 is a chart showing the excitation spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 6 is a chart showing the reflection spectra of the oxynitride phosphors of Examples 1 to 5;

Fig. 7 is an SEM photo photographing the oxynitride phosphor of Example 1;

Fig. 8 is a plane view showing the light-emitting element related to the present invention;

Fig. 9 is a section view showing the A-A' of the light-emitting element related to the present invention;

Fig. 10 is a chart showing the luminescence spectrum of the light-emitting device of Example 1 related to the present invention;

Fig. 11 is a chart showing the chromaticity coordinate of the light-emitting device of Example 1 related to the present invention;

Fig. 12 is a chart showing the cap type light-emitting device of Example 3 related to the present invention;

[EXPLANATIONS OF NUMERALS]

- 1: substrate
- 2: semiconductor layer
- 3: electrode
- 4: bump
- 10: light emitting element
- 11: phosphor
- 12: coating member
- 13: lead frame
- 13a: mount lead
- 13b: inner lead
- 14: electro-conductive wire
- 15: mold member
- 101: light emitting element
- 102: lead electrode
- 103: insulation seal member
- 104: electro-conductive wire
- 105: package
- 106: rid
- 107: window portion
- 108: phosphor
- 109: Coating member
- 201: Substrate
- 202: groundwork layer

203: n-type layer
203a: exposed plane
204: active layer
205: p-side carrier confining layer
206: first p-layer
207:
208: p-side contact layer
209: light emission portion
210: p-side electrode
210a: electrode branch
210b: p-side pat electrode
211a: n-side electrode
211b: n-side pat electrode

Fig. 1

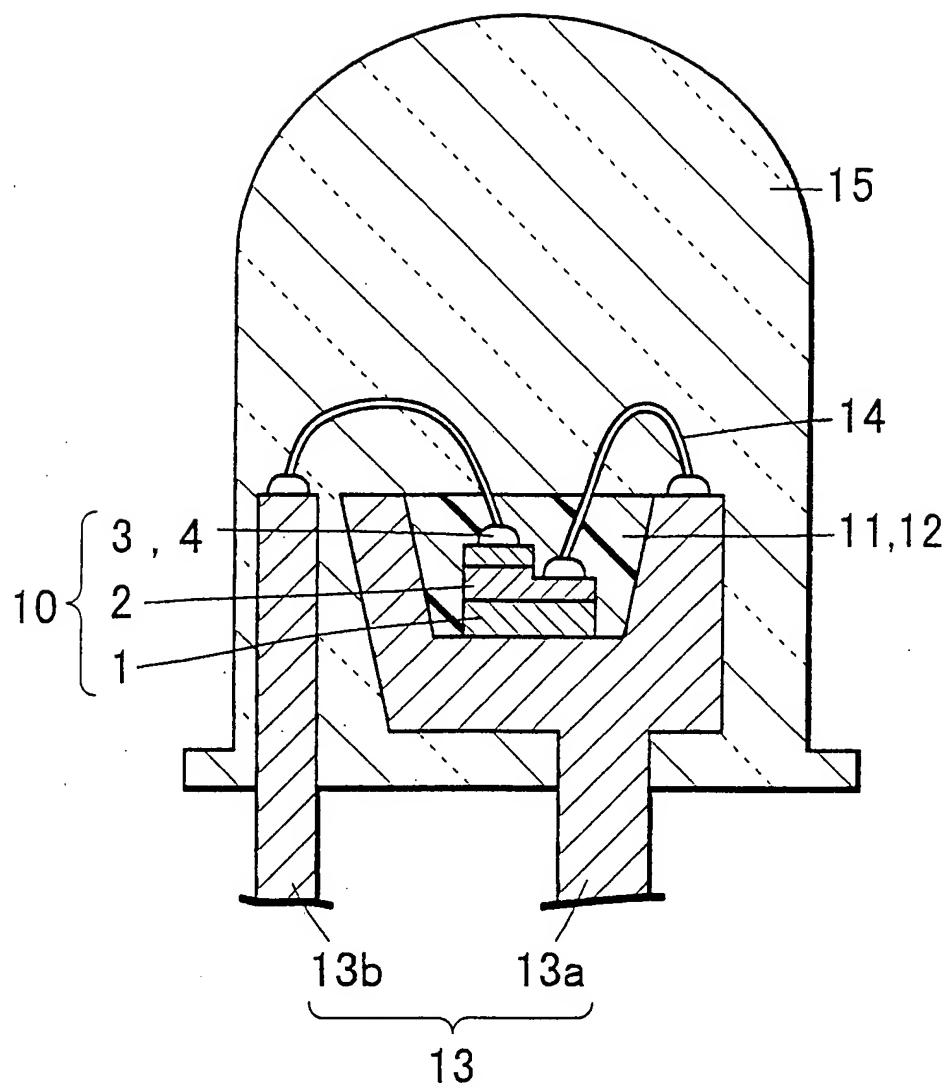
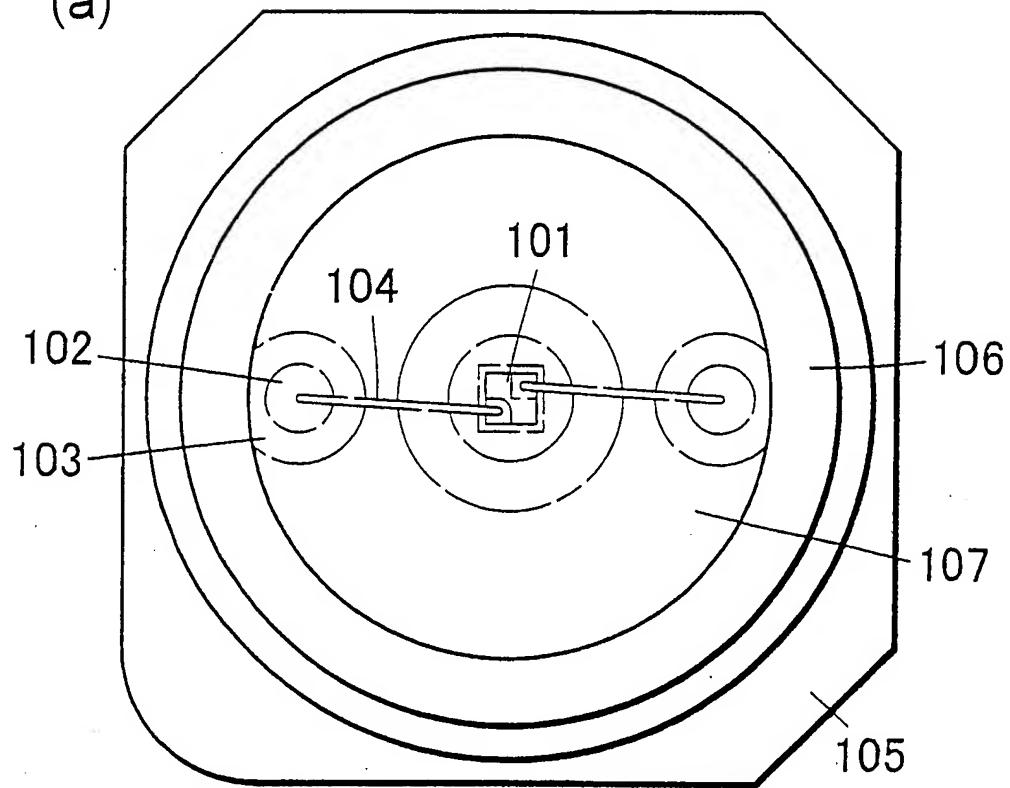


Fig. 2

(a)



(b)

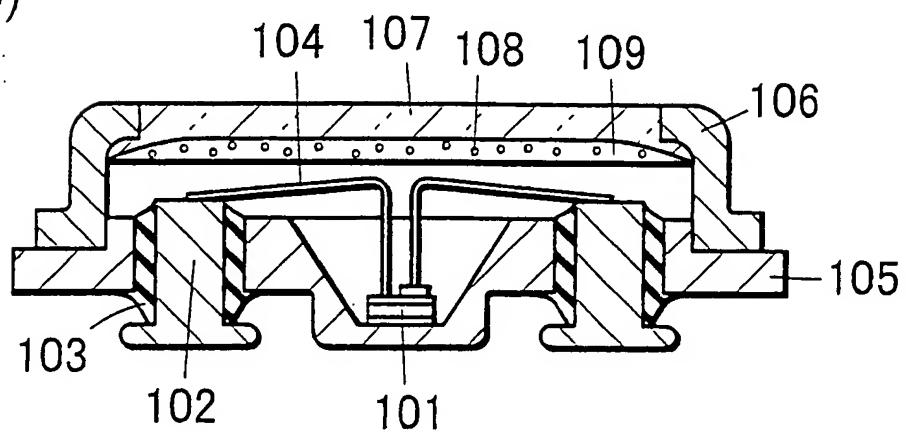


Fig. 3

Luminance spectra (Ex400nm)

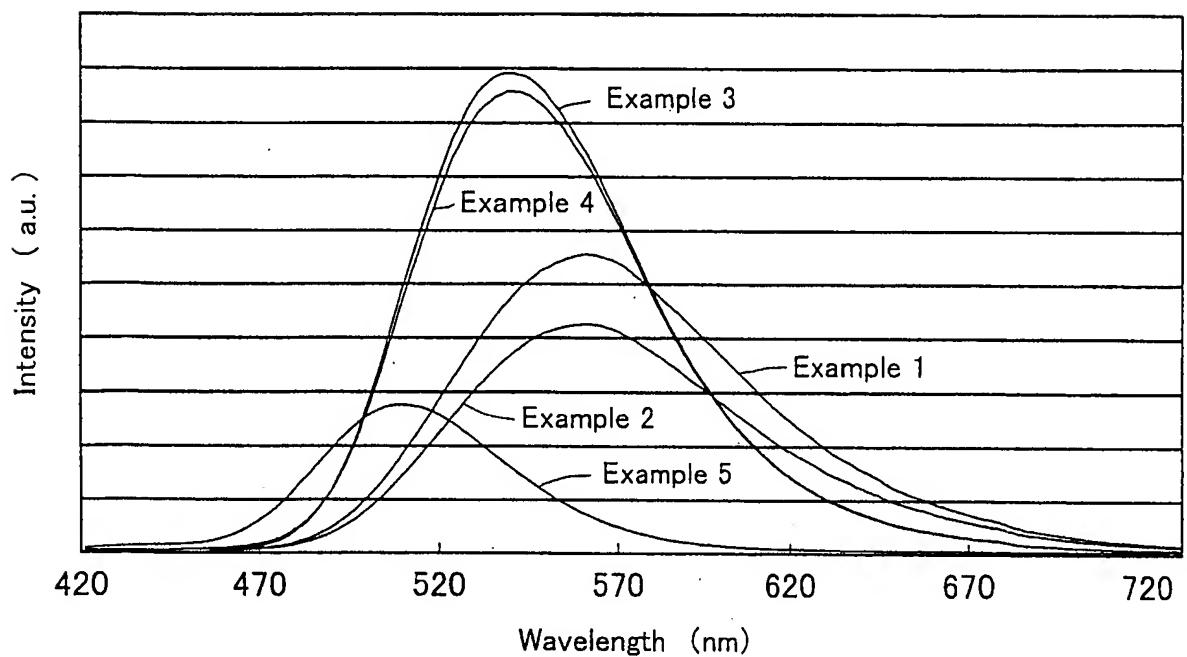


Fig. 4

Luminance spectra (Ex400nm)

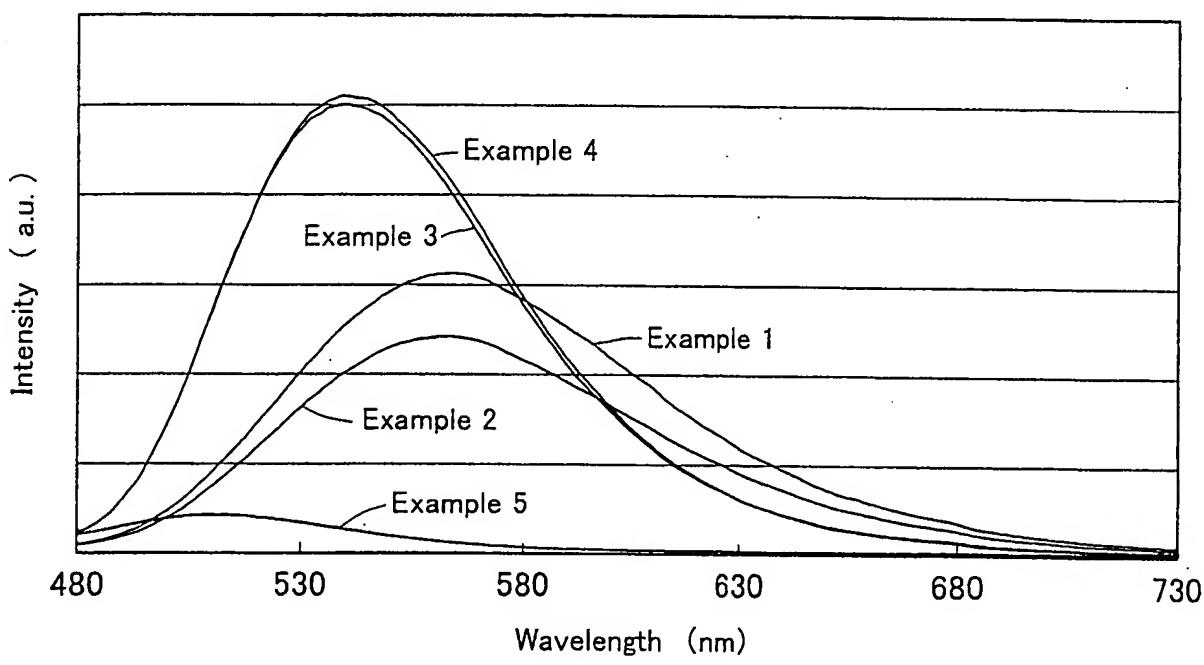


Fig. 5

Excitation spectra

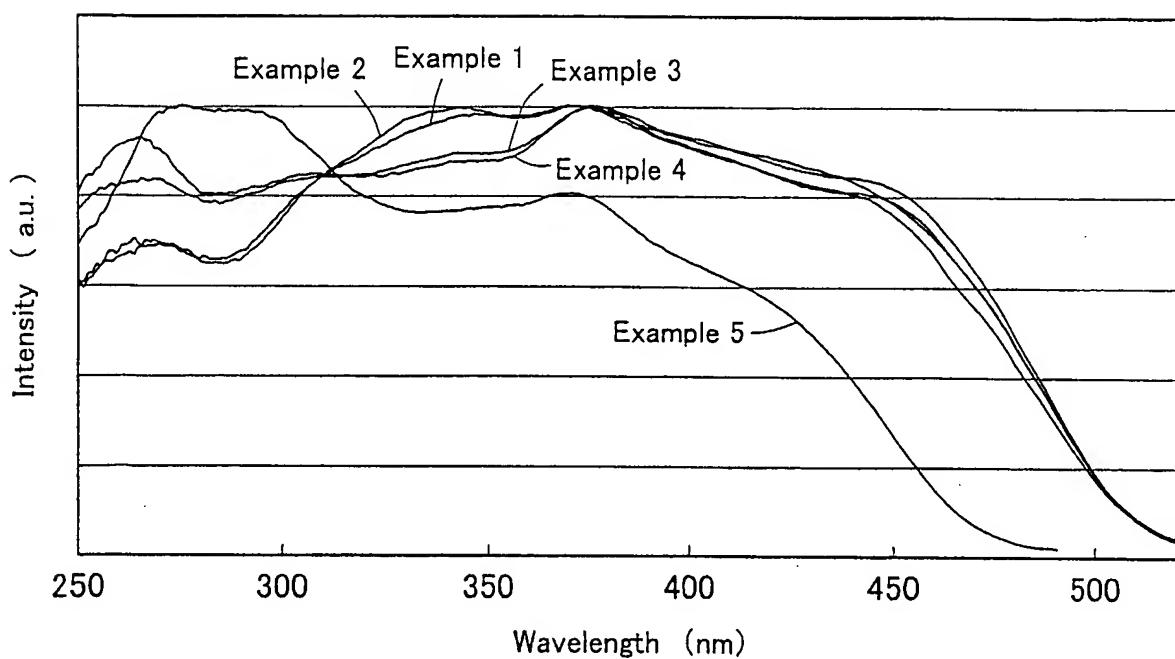


Fig. 6

Reflection spectra

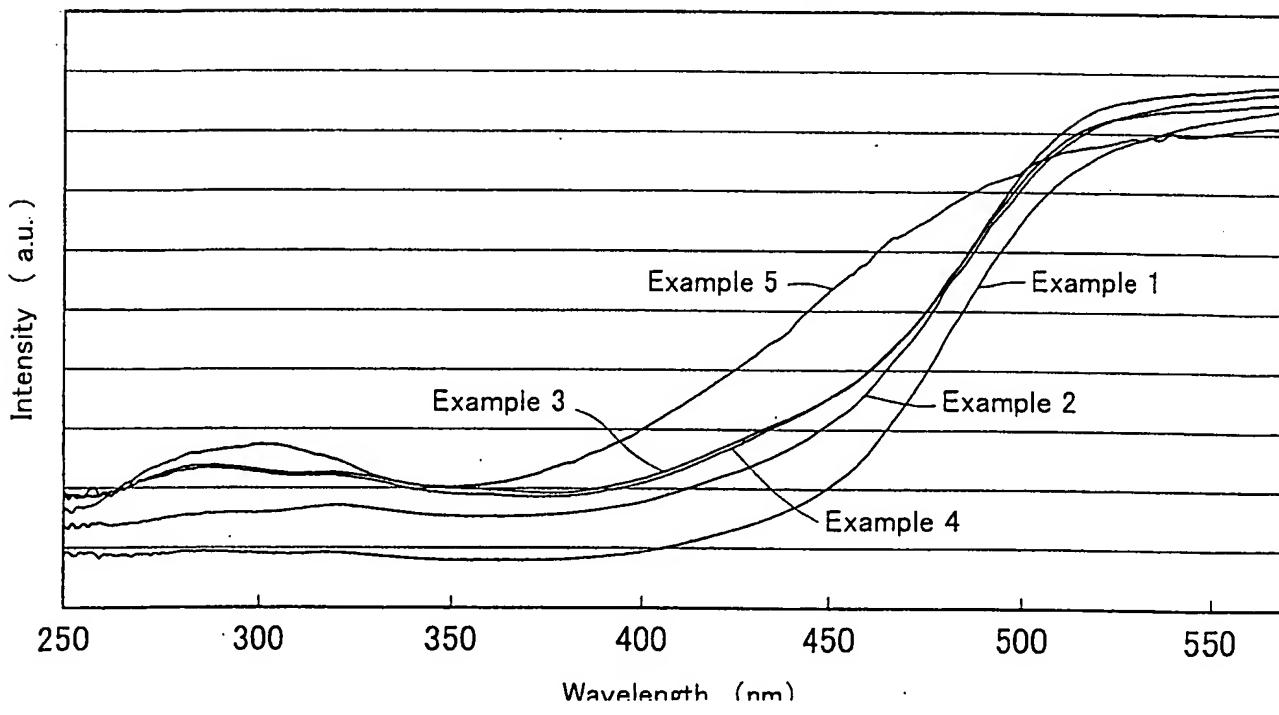
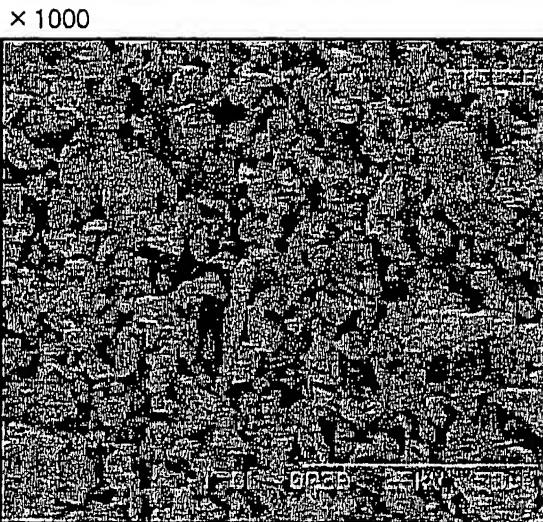


Fig. 7

(a)



(b)

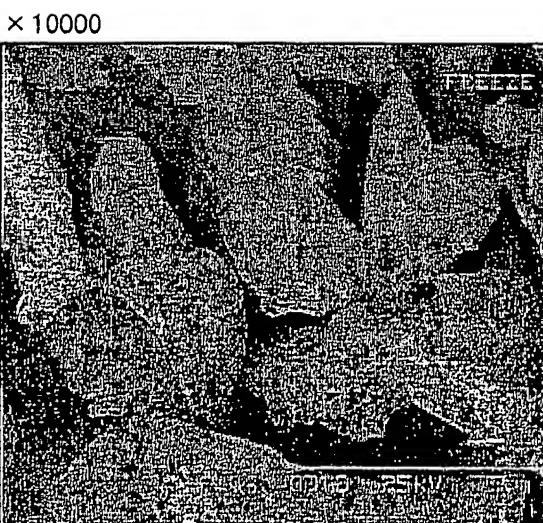


Fig. 8

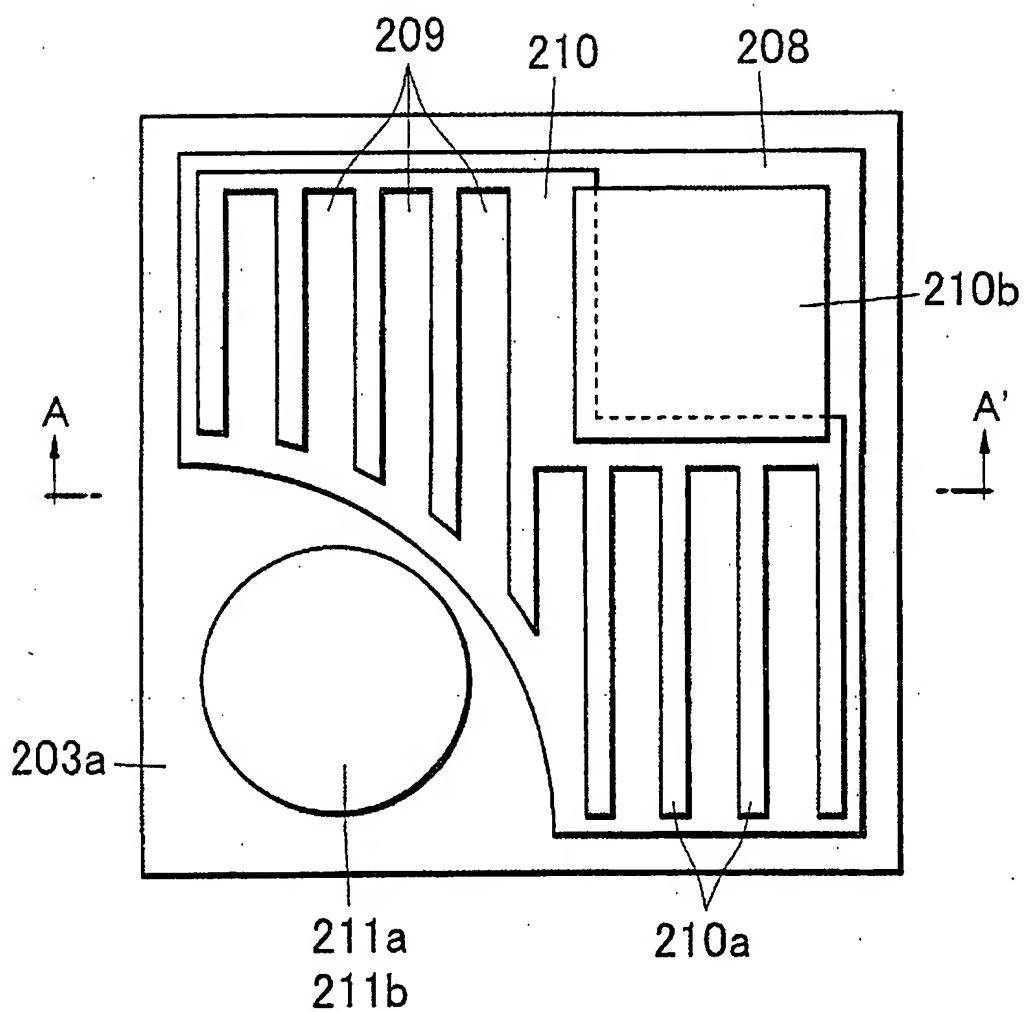


Fig. 9

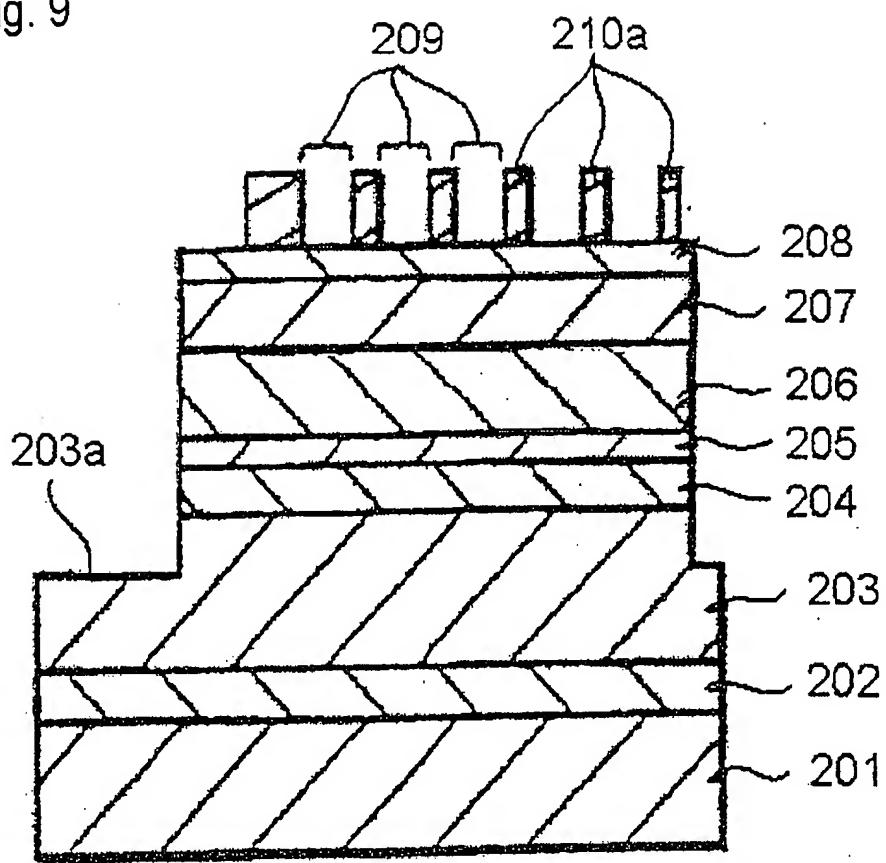


Fig. 10

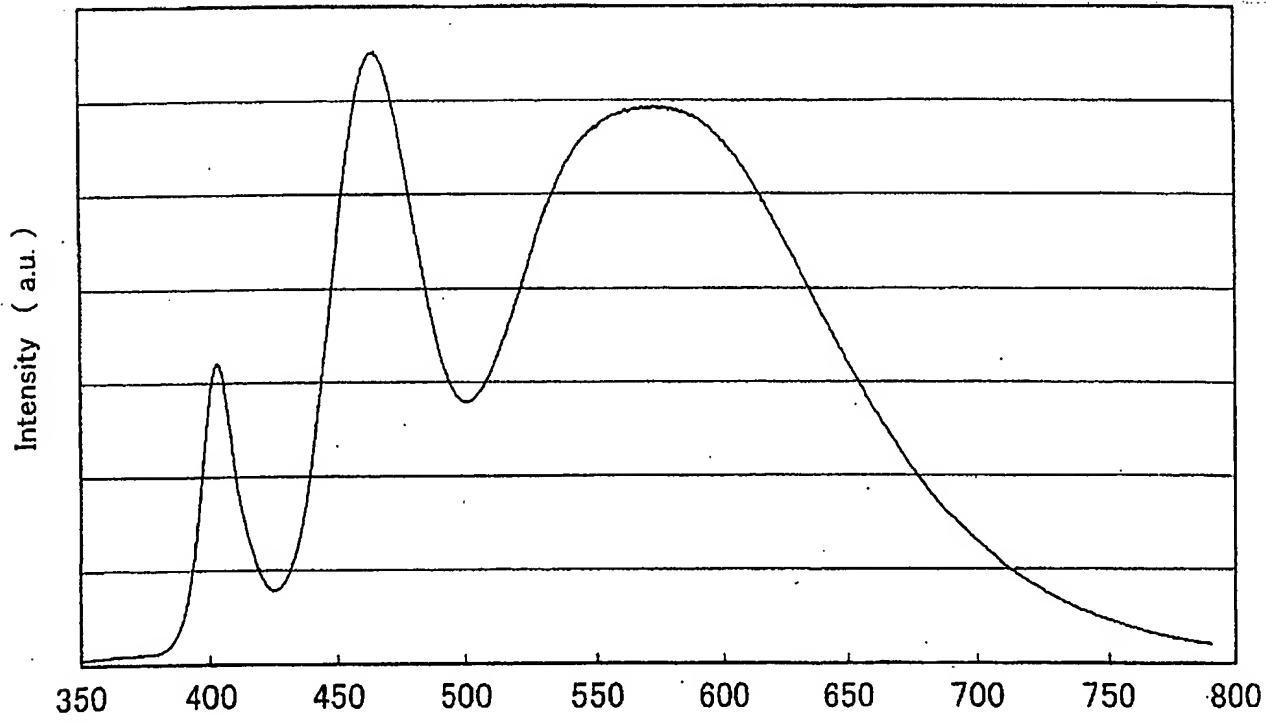
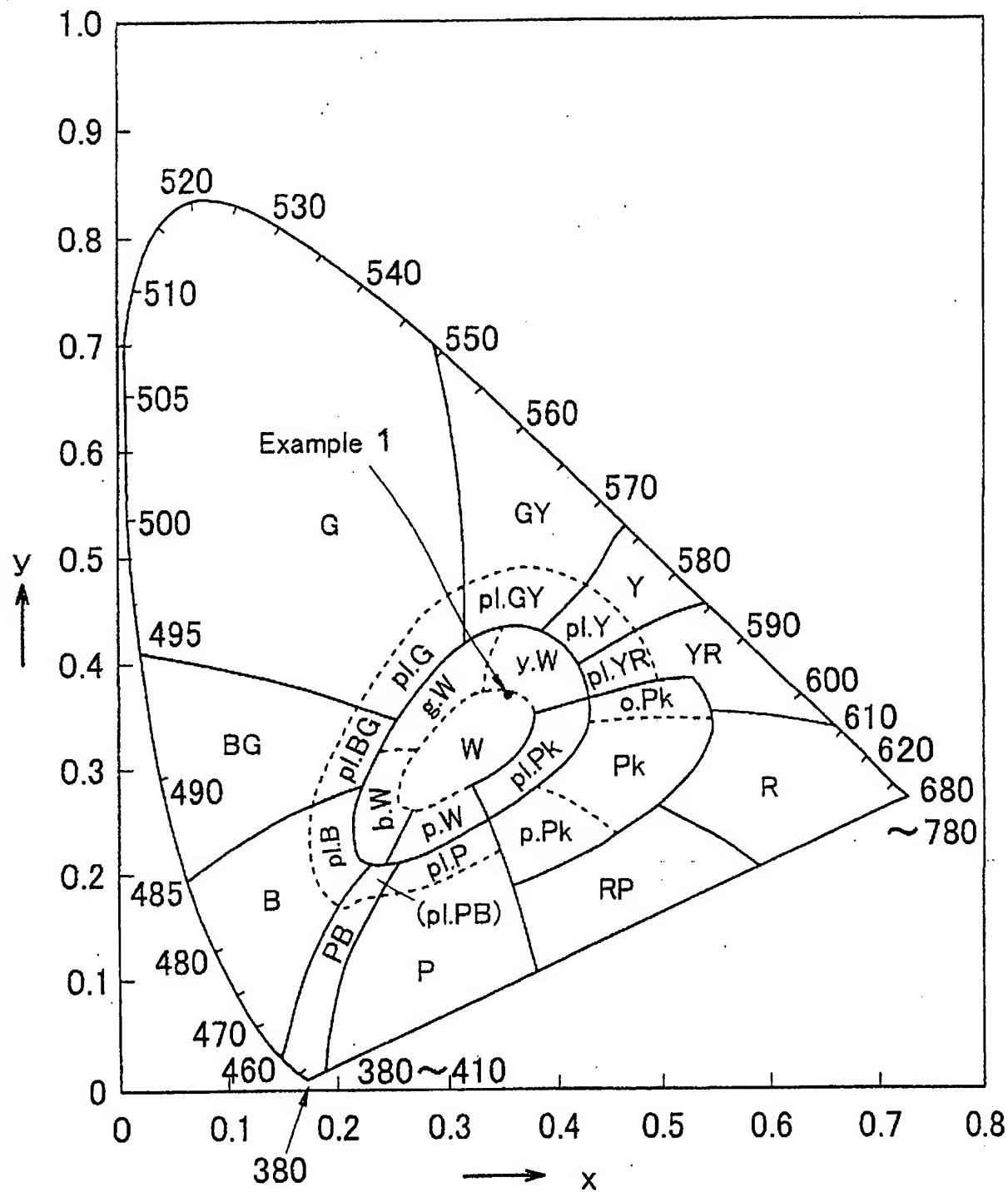
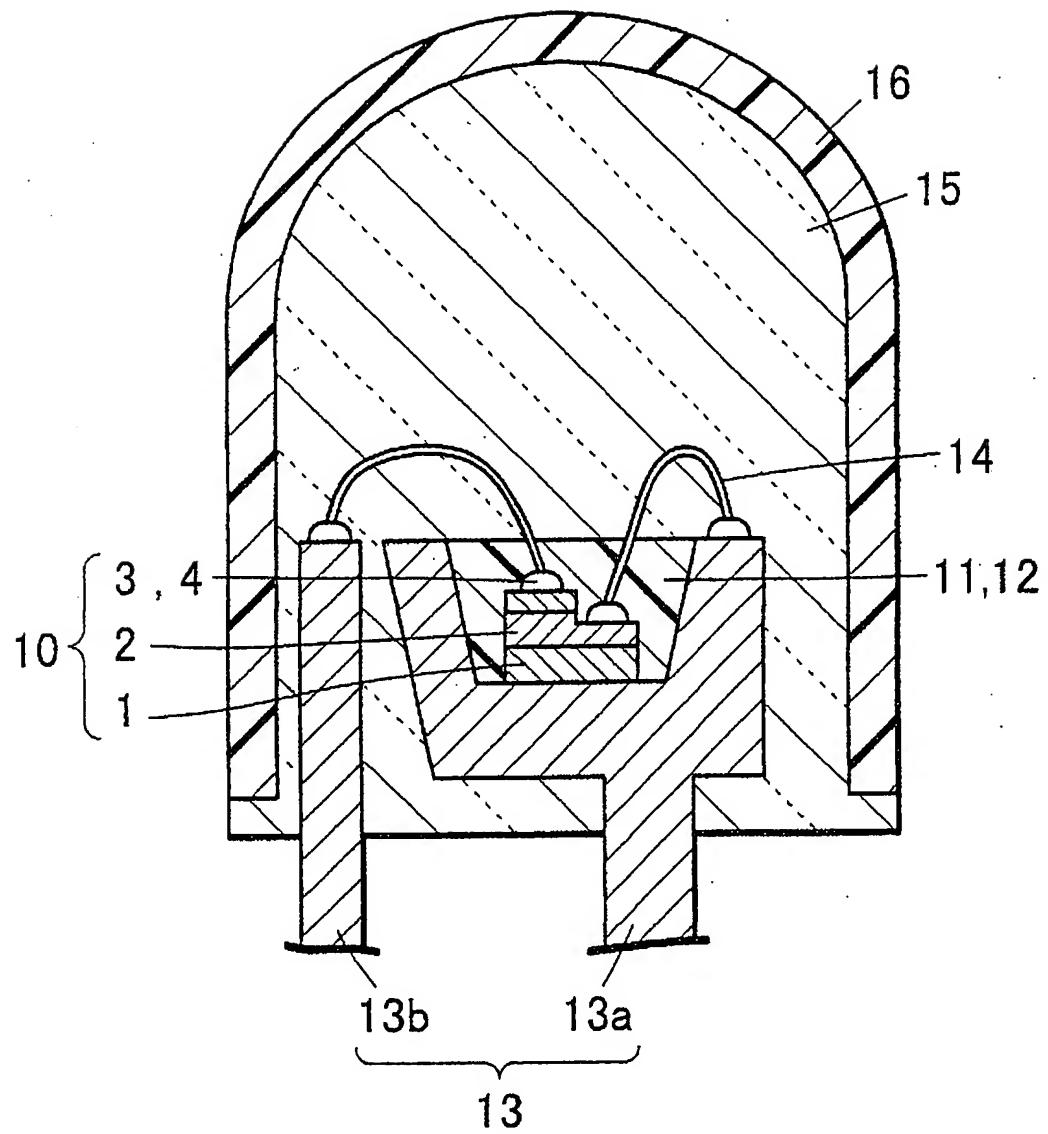


Fig. 11



G : Green	GY : Yellow green	pl.Y : pale yellow	b.W : Bluish white
Y : Yellow	YR : Yellow red	pl.G : pale green	g.W : Greenish white
R : Red	RP : Red purple	pl.B : pale blue	p.W : Purplish white
B : Blue	BG : Blue green	pl.P : pale purple	y.W : Yellowish white
W : White	PB : Blue purple	pl.Pk : pale pink	o.Pk : Orange pink
P : Purple	Pk : Pink	pl.PB : pale blue purple	p.Pk : Purplish pink
		pl.GY : pale yellow green	
		pl.BG : pale blue green	
		pl.YR : pale yellow red	

Fig. 12



[DOCUMENT] ABSTRACT

[Abstract]

[Problem to be solved] To provide an optical disk-reproducing method and a device therefor.

[Solution] In the optical disk-reproducing method and the device therefor, a light beam reflected from the data-bearing face of an optical disk is divided into a center light area and the outside light area in the direction corresponding to the radial direction of the optical disk, and detected; a first detecting signal to the center light area and a second detecting signal to at least the outside light area are outputted; the sizes of the first detecting signal and/or the second detecting signal are adjusted; a reproducing signal is detected by differentially moving the first detecting signal and the second detecting signal to each other, at least one of which is adjusted in size; and a high-quality reproducing signal can be detected in the reproduction of the optical disk having width-changeable tracks.

[Selected Figure] Fig. 10

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